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HYDROGEN TRANSPORT IN COPPER

by

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### Abstract

Hydrogen interaction with oxygen in copper exerts a significant influence on the apparent hydrogen diffusivity and the quantity of hydrogen absorbed. This interaction associated with steam embrittlement has been well established in alloys with high oxygen contents, such as electrolytic tough pitch (ETP) copper. However, the importance of this interaction on hydrogen transport in 99.999% oxygen-free, high conductivity (OFHC) copper and boron-deoxidized (BD) copper apparently has not been recognized. Correlation of the amount of absorbed tritium with oxygen content and dependence of permeation transients on both oxygen content and prior treatment indicate that both reversible and irreversible interactions occur between hydrogen and dissolved oxygen.

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## Introduction

Hydrogen embrittlement of copper has been generally attributed to formation of voids generated by reaction between diffusing hydrogen and cuprous oxide inclusions.<sup>1</sup> Susceptibility to hydrogen embrittlement, however, does not require cuprous oxide inclusions, but can also result from the reaction of hydrogen with oxygen in solution.<sup>2</sup> Furthermore, impurity oxides that are reduced by hydrogen and impurity elements, such as arsenic, antimony, or bismuth, that form volatile hydrides upon reaction with hydrogen may contribute to embrittlement.<sup>2</sup>

Intergranular void formation and subsequent cracking is most pronounced above the critical point of water, 647°K, where the reaction



forms steam.<sup>1</sup> At lower temperatures embrittlement develops more slowly.<sup>3</sup> Embrittlement has been described as a two-stage process of incubation followed by cracking, with oxygen diffusion to internal surfaces being the rate-controlling mechanism during the incubation stage and hydrogen permeation from the external surface to the internal voids being the rate-controlling step in the cracking stage.<sup>4</sup>

The several varieties of embrittlement that have been observed attest to a strong attractive interaction between the diffusing

hydrogen and oxygen that is present either as a reducible oxide (e.g.,  $\text{Cu}_2\text{O}$ ,  $\text{MnO}_2$ ,  $\text{NiO}$ ) or in solution. The interaction of hydrogen with dissolved oxygen has been observed in other metals and has also been studied intensively in the niobium-hydrogen-oxygen system.<sup>5,6,7</sup> A similar attractive interaction is apparent with arsenic, antimony, and bismuth. All of these elements, therefore, would be expected to influence hydrogen diffusion in copper by acting as trapping sites. Such a trapping effect would extend to temperatures below the range where embrittlement is detected and should affect both transient permeation and absorption behavior.

Interaction between dissolved hydrogen and lattice imperfections has been observed in several experiments with copper; likewise, such imperfections serve as trapping sites. Vacancy-hydrogen interaction was inferred from recovery of electrical resistivity in high-purity copper wires quenched from elevated temperatures following hydrogen annealing.<sup>8</sup> The activation energy for recovery at  $193^\circ\text{K}$  was approximately the same as for hydrogen diffusion. An internal friction peak at  $150^\circ\text{K}$  was attributed to the hydrogen-dislocation interaction.<sup>9</sup>

Deuterium permeation experiments and tritium absorption studies on several grades of commercial copper, as well as high-purity copper, provide evidence for trapping of hydrogen. The effects correlate with oxygen content indicating that the H-O interaction has a significant effect on hydrogen transport.

## Results

### *Deuterium Permeation*

Deuterium permeation measurements were made on both oxygen-free (OF) and boron-deoxidized (BD) copper, as well as on two varieties of high-purity copper, namely, 99.999% purity from ASAR Co. and 99.99% (VP Grade) from Materials Research Corporation. Measurements were made on 0.02-cm-thick specimens of cold-rolled foil with 0.1 - to 0.5-MPa deuterium pressure over the temperature range 375 to 750°K by techniques described previously.<sup>10</sup> All of the calculated steady-state permeability values (Figure 1) fall within a fairly narrow band that is described by the relation

$$\phi = 4.14 \times 10^{-3} \exp(-17,125/RT), \frac{\text{cc}}{\text{sec}} \cdot \frac{\text{cm}}{\text{cm}^2 \sqrt{\text{atm}}}$$

with a correlation coefficient of >0.99.

Because of the large oxygen content in electrolytic tough-pitch (ETP) copper, permeation experiments are generally not feasible. At temperatures over about 650°K, voids form, and at lower temperatures, steady-state is not achieved in a reasonable time. One specimen of ETP copper was allowed to come to steady state at 800°K in about 24 hours. The specimen was then outgassed. The permeability was  $1.25 \times 10^{-7}$  (cc/sec) (cm/cm<sup>2</sup>√atm), which agrees with data for other copper alloys. However, the specimen was severely blistered (Figure 2).

Steady-state permeation rate measurements were also made on tubes of oxygen-free (OFHC) copper containing tritium gas at 299 to 373°K. A deuterium-tritium gas mixture of 22% T<sub>2</sub> was introduced

into the tubes at 69 MPa pressure, and the permeation rate of tritium was measured with both a proportional counter and an ionization chamber connected to a vibrating-reed electrometer. Results yield a higher activation energy than that obtained from published permeability data with hydrogen or deuterium. The present deuterium and tritium permeability measurements are compared with published data on hydrogen in Figure 3.<sup>11-17</sup> Although activation energies vary from 12.5 to 22.1 kcal/mol, the permeabilities all lie within a fairly narrow band after adjusting the tritium and deuterium data for isotopic mass by multiplying the measured value by the square root of the mass number.

#### *Diffusivity*

Diffusivities may be calculated from the transient permeation and evolution curves by the relations

$$P_t/P_\infty = 1 + \sum_{n=1}^{\infty} 2(-1)^n \exp(-D^*n^2\pi^2t/a^2)$$

$$\text{and } E_t/P_\infty = \sum_{n=1}^{\infty} 2(-1)^n \exp(-D^*n^2\pi^2t/a^2)$$

where  $P_t$  and  $E_t$  are the permeation and evolution rates at time  $t$ ;  $P_\infty$  is the steady-state permeation rate;  $D^*$  is the apparent diffusivity;  $a$  is specimen thickness. If there are no surface effects or trapping phenomena present, apparent diffusivities calculated by these relations will be independent of  $(P_t/P_\infty)$  and  $(E_t/P_\infty)$  and will correspond to the lattice diffusivity.

In copper, diffusivities calculated from the permeation transient are subject to fairly large variations, and the transients normally are not reproducible if the specimen has had no prior exposure to hydrogen. As the permeation-offgassing sequence is repeated, the transients shift toward shorter times but only become reproducible after several repetitions, as illustrated in Figure 4. In contrast, offgassing curves are usually quite reproducible. This behavior is probably associated with both the oxide films on the surfaces of the specimen and reaction of the permeating hydrogen with dissolved oxygen or oxide inclusions. Additional evidence for the sensitivity of the permeation transient to oxygen is shown by the shift in behavior toward longer times following a one-hour anneal in tank argon at 875°K (Figure 5). The argon had not been purified and contained small quantities of oxygen and hydrocarbons. There was a pronounced shift to longer time for the test immediately after the anneal (Curve 3).

Deuterium diffusivities calculated from the offgassing transients lie below extrapolations of previously published data (Figures 6 and 7)<sup>17-22</sup> and have a larger activation energy. The published deuterium diffusivities were obtained from outgassing experiments on single crystals saturated at an elevated temperature. The other published data were obtained using protium; however, they also lie above the present data, after correction for the isotope effect is made by the inverse-root mass relation. This

observation of lower diffusivities from permeation experiments than from outgassing of saturated specimens has also been made on nickel<sup>2,3</sup> and appears to be a characteristic of systems in which trapping occurs. Furthermore, when diffusivities are calculated for both approach to steady-state ( $P_t/P_\infty = 0.90$ ) and offgassing afterwards ( $E_t/P_\infty = 0.966$ ), the results differ and diverge as the temperature is lowered.

### *Solubility*

Tritium solubility in copper was measured in two experiments: several grades of copper rod were exposed to mixed deuterium-tritium gas at 450°K for 34 days at 69 MPa (total gas pressure at room temperature); four grades of copper rod were exposed to tritium gas at 535°K for 260 hours at ~0.1 MPa. Included in these experiments were deoxidized, low-phosphorous (DLP) copper; deoxidized, high-phosphorous (DHP) copper; and "AMPHOS,"\* a low phosphorous alloy based on OF copper. Tritium concentrations in the exposed rods were measured by liquid scintillation counting of solutions obtained by acid dissolution of the specimens. In the first case, the whole rod was dissolved, and an average tritium content was measured. The second set of specimens were dissolved incrementally to determine concentration profiles.

Measured tritium contents in the exposed rods correlate with the nominal oxygen content, as seen in Figure 8, a result that is

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explicable in terms of an attractive hydrogen-oxygen interaction in copper. Two data points lie below the band. These low values are for ETP copper at 0.1 MPa near the centers of the rods and result from failure to saturate the specimens because of the trapping near the surface induced by the high oxygen content. These values are approximately the same tritium content as for the 99.999% Cu and correspond to the concentration  $7.6 \times 10^{-5}$  cc H<sub>2</sub>/cc Cu calculated from the results of McLellan,<sup>24</sup> which were obtained with hydrogen on spheres of high-purity copper at higher temperatures.

Exposure times were adequate in both experiments to saturate the specimens if no reaction between hydrogen and oxygen had occurred. The concentration profiles (Figure 9) indicate this was true for those copper specimens with only 10 ppm oxygen (99.999 OF and BD), but not for ETP copper, which contains ~200-400 ppm oxygen. The surface concentration was about 1-4 cc T<sub>2</sub>/cc Cu in every case, indicating a high oxygen content near the specimen surface. Tritium contents dropped abruptly to the normal level at  $X/r \approx 0.93$  to  $0.99$  except for ETP copper where high tritium levels penetrated to  $X/r \approx 0.75$ . This profile may be duplicated approximately by a modified McNabb-Foster trapping model ( $\mu = 0$ ) with  $D = 1.6 \times 10^{-10}$  cm<sup>2</sup>/sec,  $C_0 = 4.06 \times 10^{15}$  cc T/cc Cu and  $N = 8.76 \times 10^{19}$  traps/cc Cu. The trap density is calculated on the basis of 260 ppm O<sub>2</sub> in the copper and each oxygen atom trapping one hydrogen atom.

## Conclusions

On the basis of the experimental evidence discussed herein, we conclude:

1. Measured hydrogen contents in "pure" copper correlate with the level of oxygen that is present. This implies that the lowest measured solubilities may be more nearly representative of the lattice solubility. Larger hydrogen contents are associated with trapping and internal porosity, sometimes on a microscale.
2. Measured diffusivity is affected by the presence of oxygen at temperatures below  $\sim 650^{\circ}\text{K}$ . Both reversible and irreversible trapping of hydrogen by dissolved oxygen apparently contribute to lowering of diffusivity below the expected value.
3. Absorption and permeation transients depend on the oxygen content; therefore, simple diffusion theory is inadequate for predicting the transient permeation behavior of hydrogen in copper. Models that incorporate trapping, such as that of McNabb and Foster, are needed to describe the transport kinetics.

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## FIGURE LIST

- FIGURE 1 - Deuterium permeability in copper.
- FIGURE 2 - Blister formation in permeation specimen of ETP copper exposed to deuterium at 800°K.
- FIGURE 3 - Permeability of copper to hydrogen isotopes.
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- FIGURE 5 - Effect of annealing in tank argon on transient permeation behavior.
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- FIGURE 7 - Diffusivity of hydrogen isotopes in copper.
- FIGURE 8 - Correlation of quantity of tritium absorbed with oxygen content of copper.
- FIGURE 9 - Tritium concentration profiles in several grades of copper at 535°K.

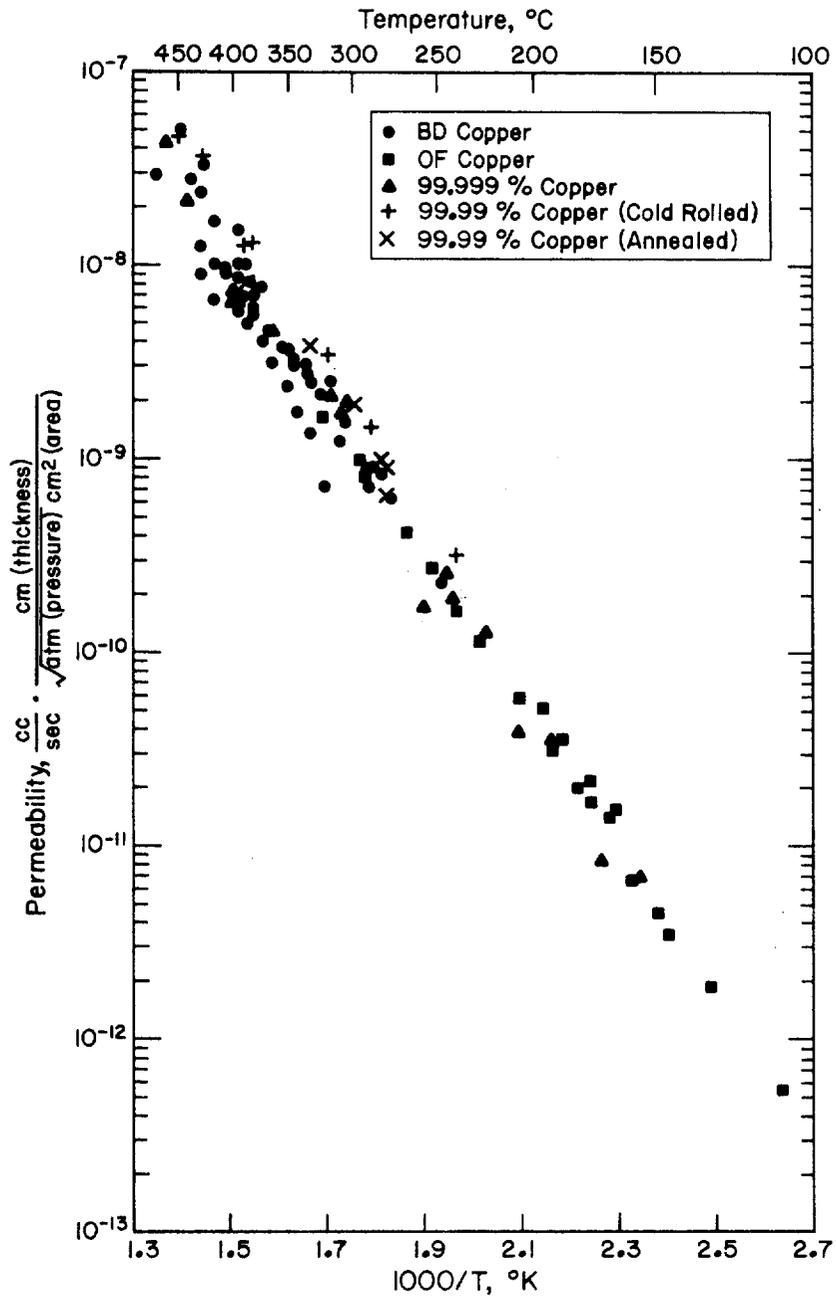


FIGURE 1 - Deuterium permeability in copper.

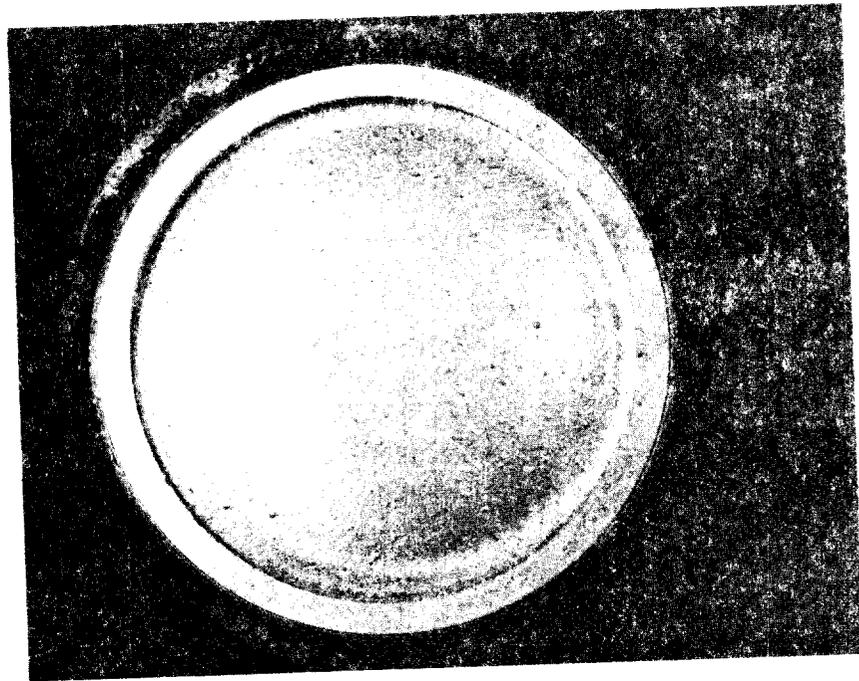


FIGURE 2 - Blister formation in permeation specimen of ETP copper exposed to deuterium at 800°K.

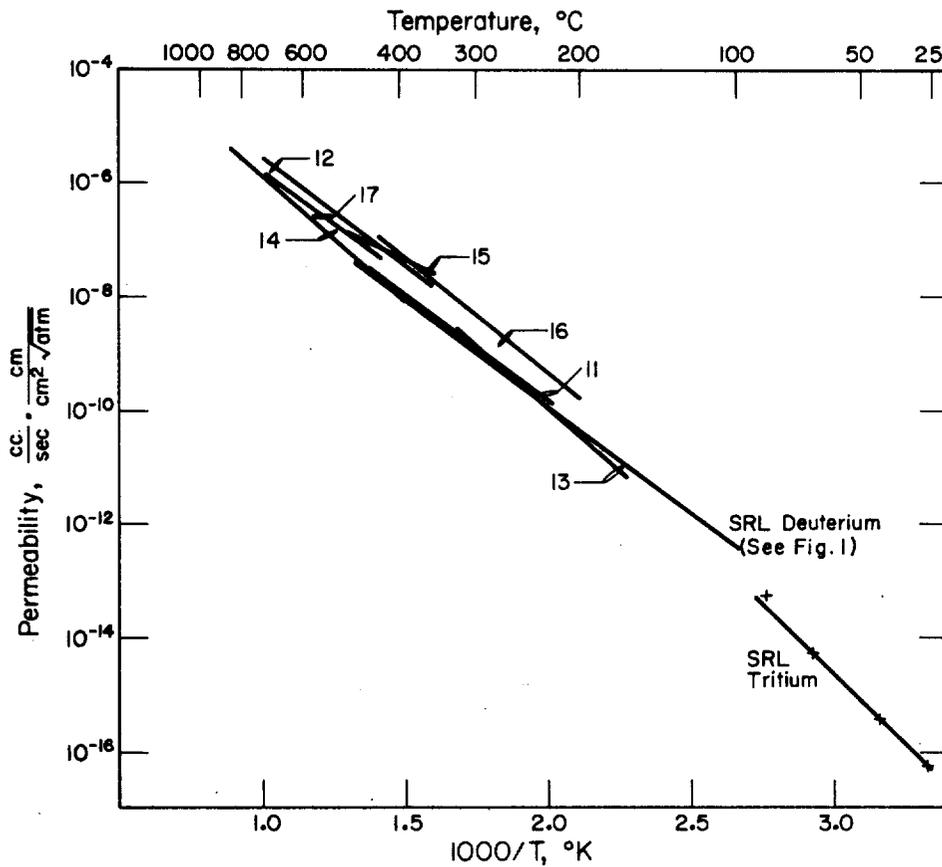


FIGURE 3 - Permeability of copper to hydrogen isotopes.

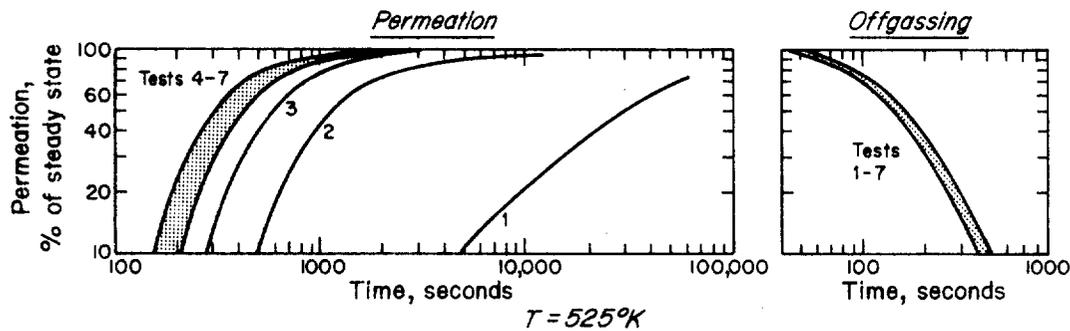


FIGURE 4 - Variation in permeation transient with repetition of test.

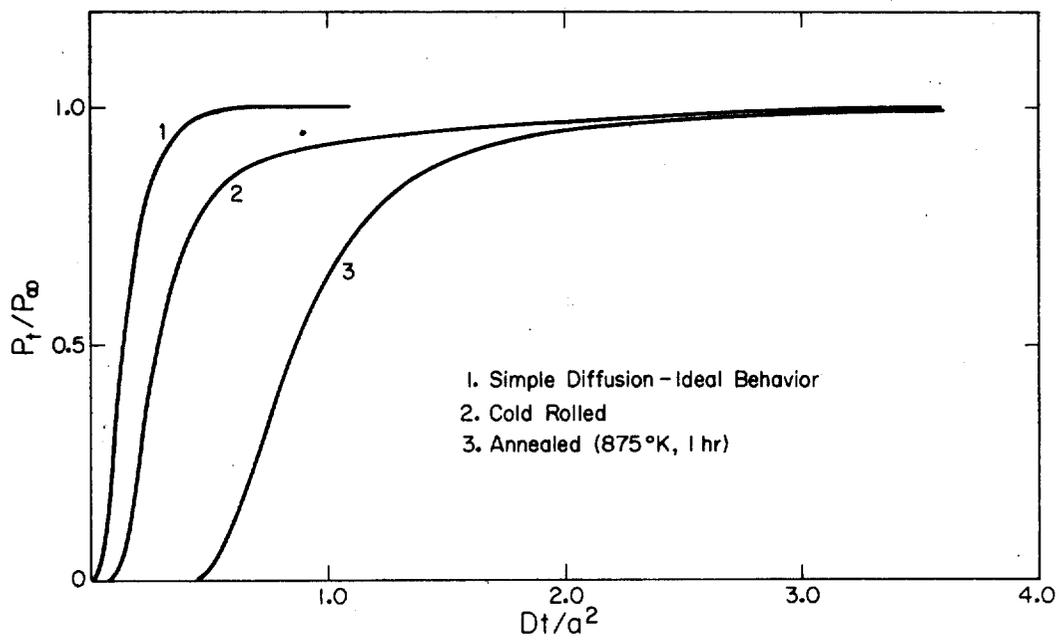


FIGURE 5 - Effect of annealing in tank argon on transient permeation behavior at 595°K.

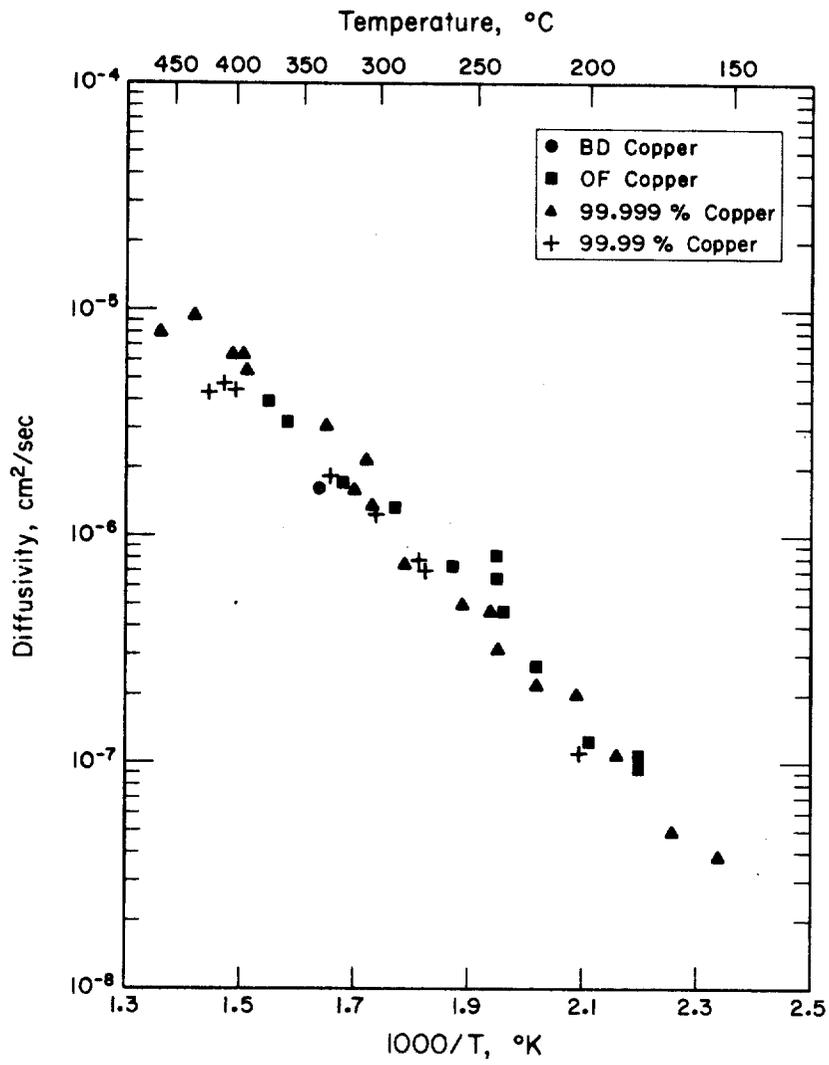


FIGURE 6 - Deuterium diffusivity in copper.

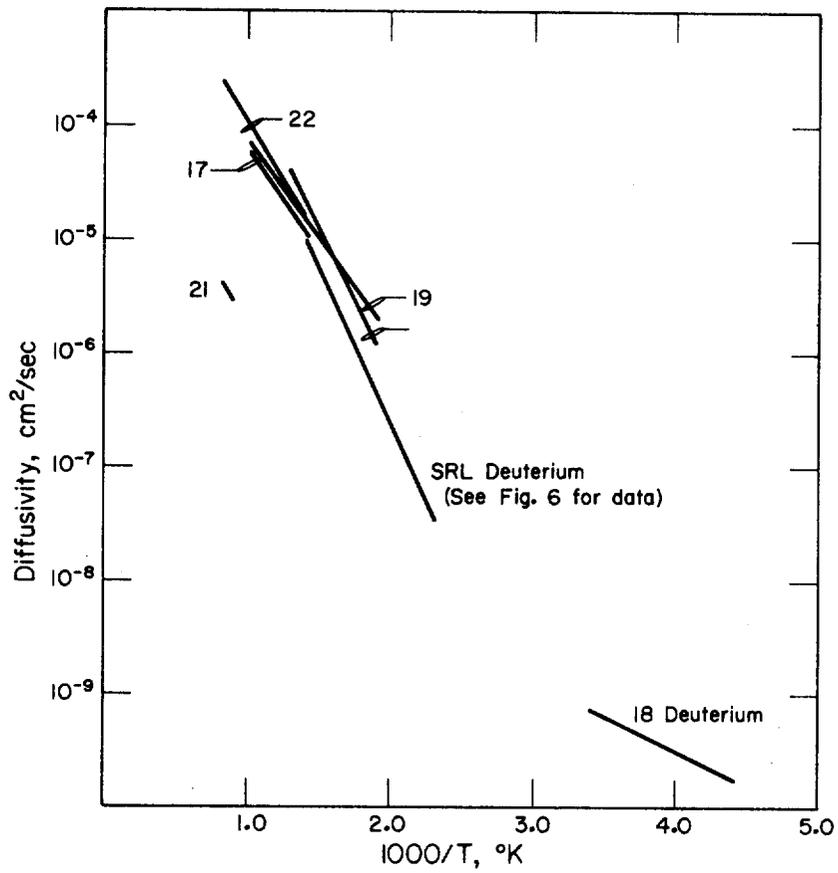


FIGURE 7 - Diffusivity of hydrogen isotopes in copper.

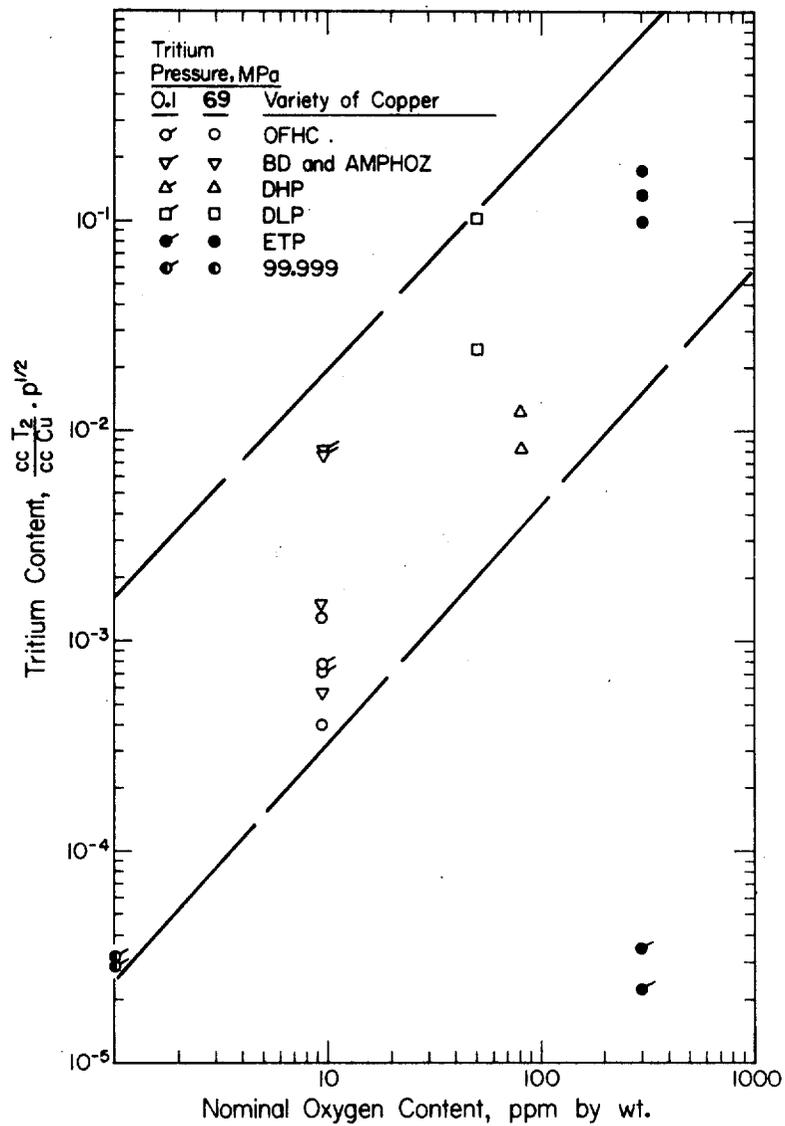


FIGURE 8 - Correlation of quantity of tritium absorbed with oxygen content of copper.

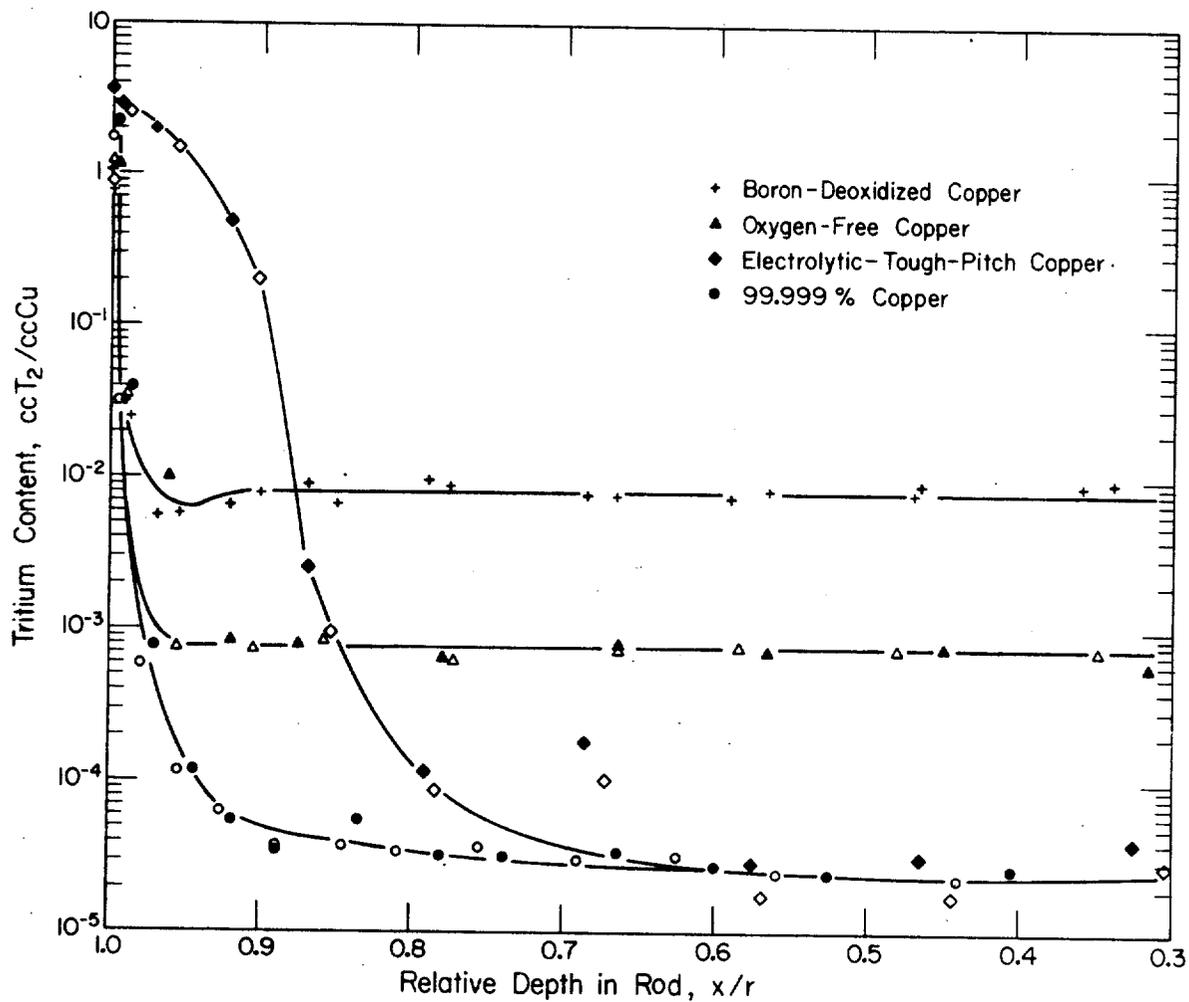


FIGURE 9 - Tritium concentration profiles in several grades of copper at 535°K.