Measurement of Helium Diffusion in Metals

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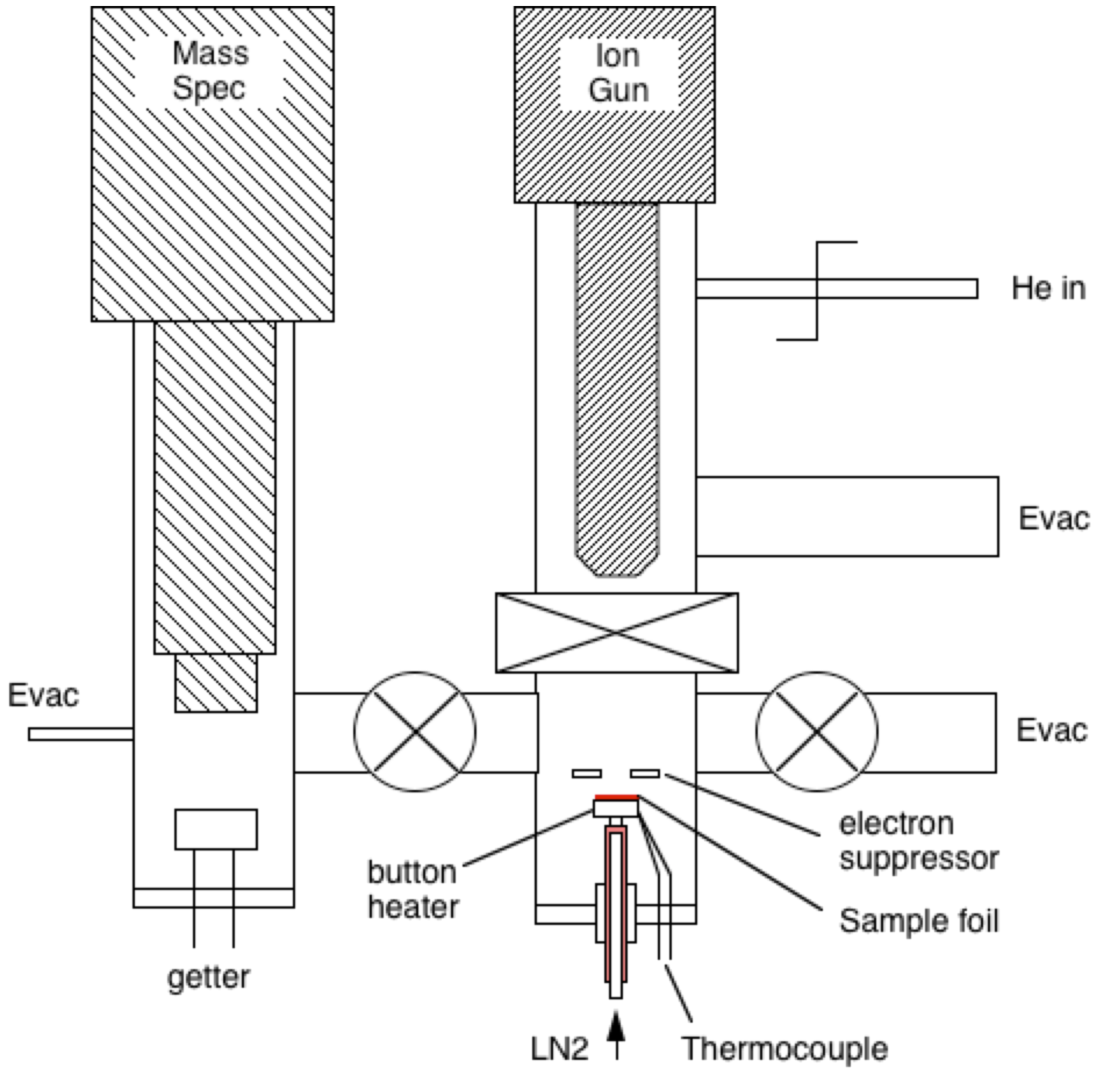
Overview

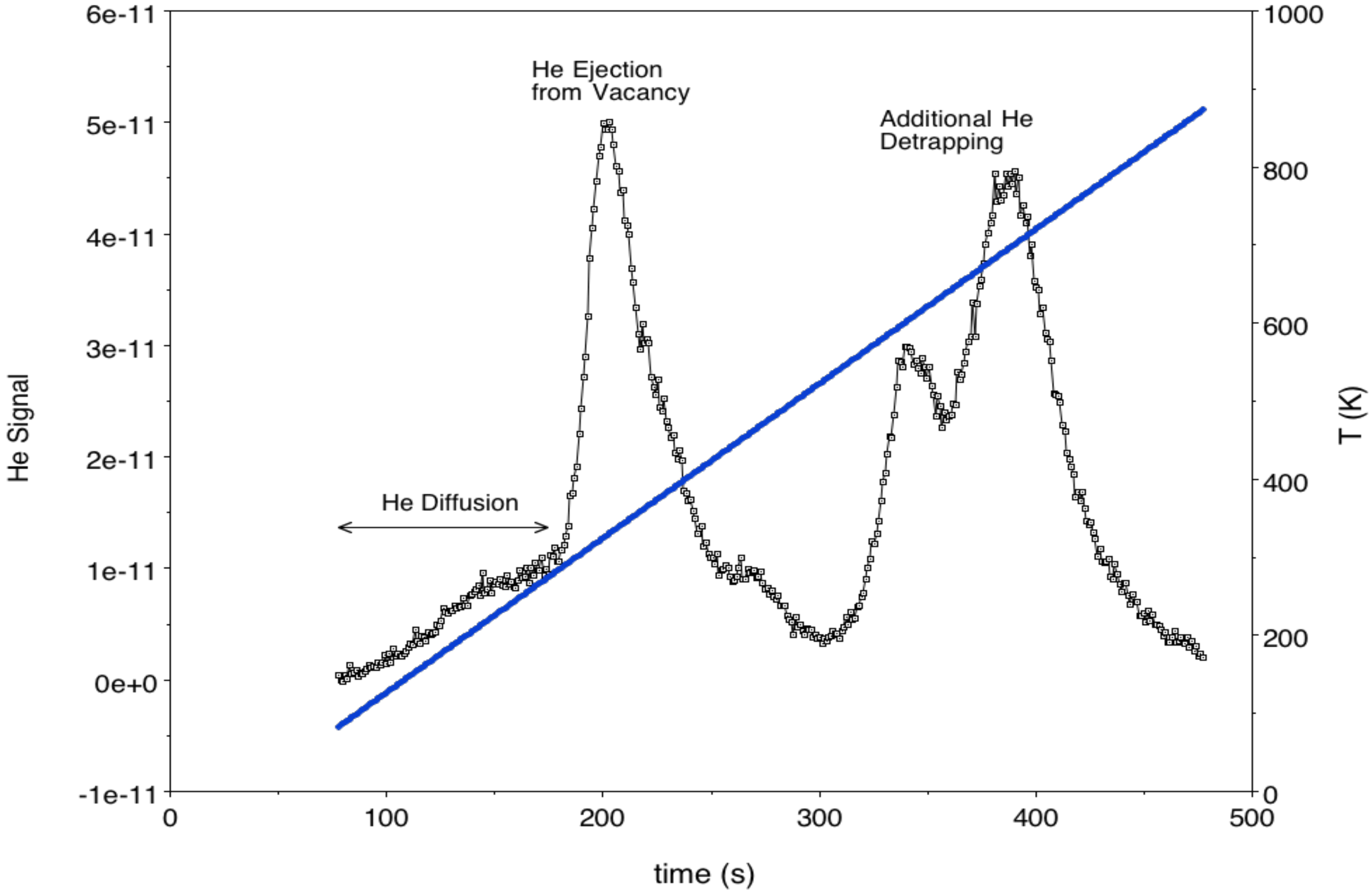
- Helium is generated in tritium exposed materials by beta decay.
- It is insoluble in metals and diffuses to the surface or collects in high-pressure bubbles, eventually affecting the materials structural integrity.
- Modeling this process requires knowledge of the effective He diffusion and trapping parameters.
- Previous efforts with He implantation have focused on bubble growth and the onset of blistering.
- Here, a new, "gentle" implantation technique is described where He clustering is reduced. It involves
  - a low energy, short He implantation pulse at low temperature
  - followed by a rapid thermal desorption ramp.
- An analytic expression of desorption behavior yields both diffusion and trapping data.
  - Fickian diffusion from slab (short time limit)
  - SRIM implantation profile
- Results: first experimental data on He diffusion in Ni, Cu, and Pd.

Experimental System



- Samples, 100 µm foils
  annealed: large grain
- He energy (0.5-5.0 keV)
  range = 4-20 nm
- Spot size, 4-6 mm
- Implant pulse (1-100 nC)
  .1-10 appm He
- Sample evacuation (20 s)
- Rapid He-TDS (1-2 K/s)

The thermal desorption spectrum shows both diffusive behavior and He release from traps



Analytic expression for diffusive desorption

- Diffusion from a plane sheet of half-thickness R (Crank, per Kass*):

$$M_t = 2\,(Dt/\pi R^2)^{1/2}\,\{\,1 + \sum \exp(-nR^2/Dt)\ \&\ \mathrm{erfc}(nR/\sqrt{Dt})\,\}$$

For small times, the release from one side, $M_t = (Dt/\pi R^2)^{1/2}$

- Crank also shows this solution for constant diffusivity D may be transformed for D(t) by replacing Dt by

$$\tau = \int_0^t D(t')\,dt'$$

- With a linear ramp $T = T_0 + \beta t$ and $D = D_0 \exp(-E_D/kT)$,

$$\tau = (D_0 k T^2/\beta E_D)\exp(-E_D/kT)$$

- Substituting, for large E_D/kT

$$M_t = (kT^2 D_0/\pi\beta R^2 E_D)^{1/2}\exp(-E_D/2kT),\qquad \text{proportional to } 1/R$$

or

$$\ln(M_t/T) = \tfrac{1}{2}\ln(kD_0/\pi\beta R^2 E_D) + E_D/2kT,\qquad \text{linear with } 1/T$$

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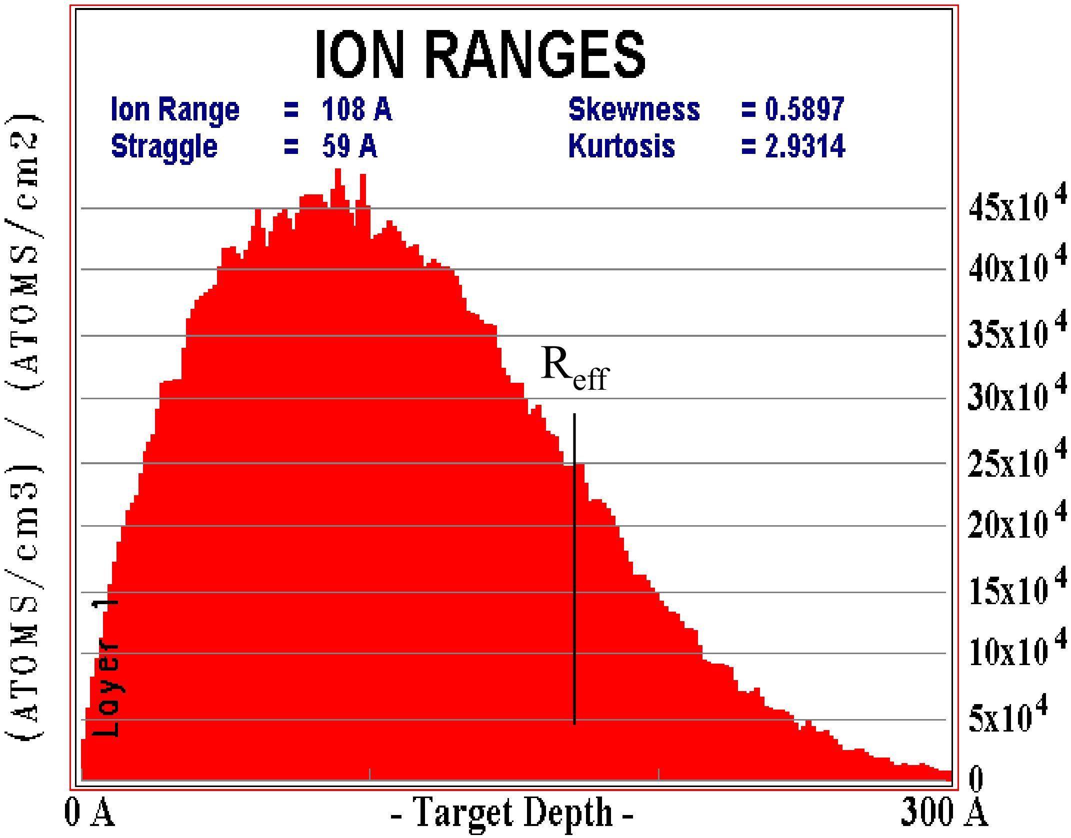
*W.J. Kass, J. Vac. Sci. Technol. 14 (1977) 518.

R is determined from Implantation Profile

SRIM: 2 keV He implantation into Pd



- For non-interacting He, the cumulative release is the sum of release from layers with R determined by *right* side of implant profile.

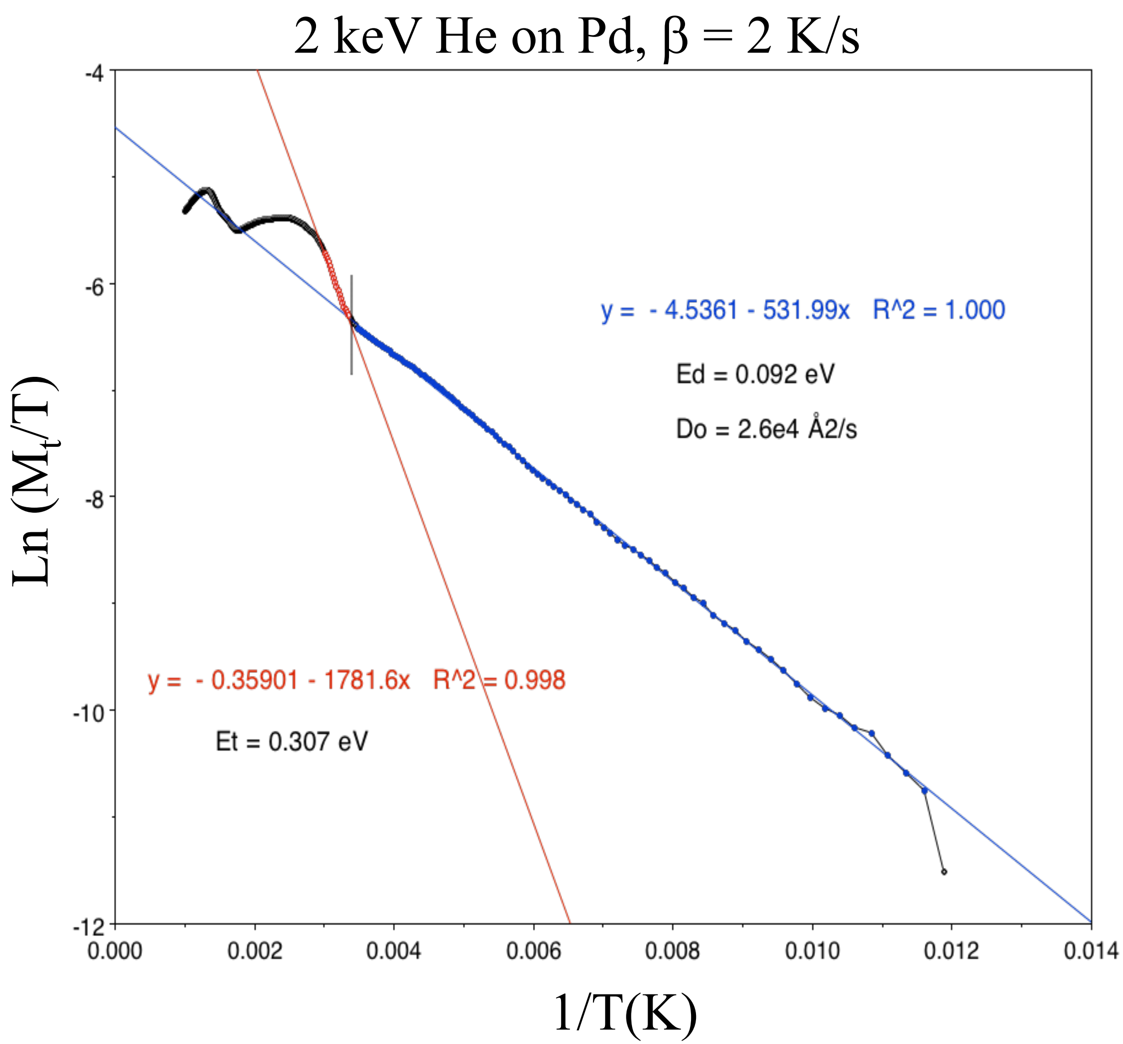
- Since $M_t \propto 1/R$, the effective thickness is

$$1/R_{eff} = (1/n) \sum_n (1/R_n)$$

2 keV He on Pd: $R_{eff} = 169$ Å

- For a 500 s spectrum, errors from the absence of release from the *left* side of the profile ($R<R_{eff}/10$) occur during the 20 s evacuation.

Typical fit to plot of Ln (M_t/T) vs 1/T



- Plot is linear over several orders.

  - From slope S, $E_D = 2kS = 0.092$ eV

  - From y-intercept I, $D_0 = 2\pi\beta R^2 S \exp(2I)$ $= 2.6$ e-12 cm^2/s

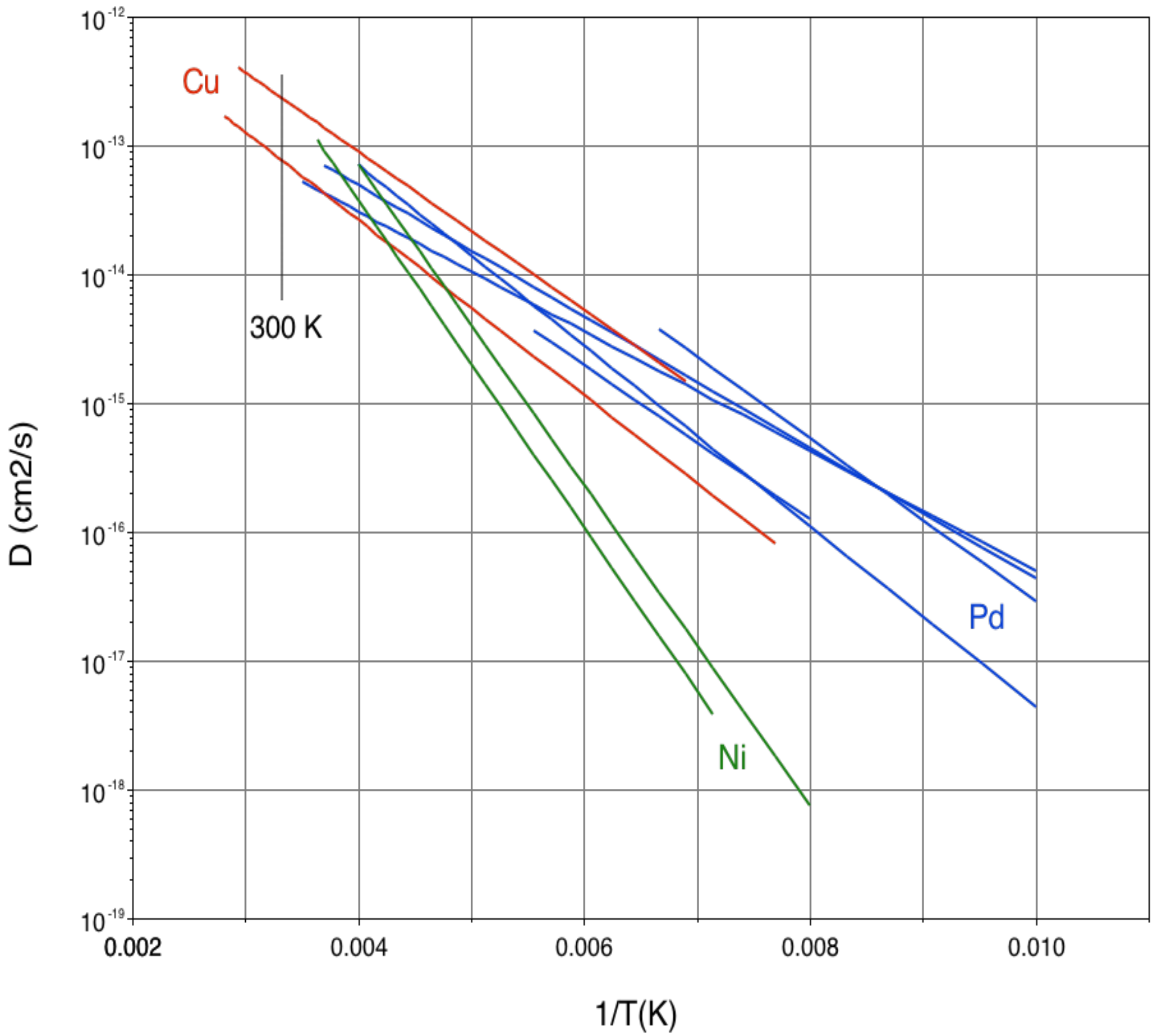
- Rapid rise yields $E_T = 0.32$ eV

  (Pd interstitial-vacancy recombination will eject He from vacancy)

Table of results

Run	E(keV)	β(K/s)	E_D(eV)	D_0(cm^2/s)	D_{300K}(cm^2/s)	E_T(eV)
Pd4d	2	2	.101	5.4e-12	1.02e-13	.381
Pd4e	2	2	.092	2.2e-12	0.62e-13	.307
Pd4f	2	2	.139	4.5e-11	2.06e-13	.349
Pd4g	2	1	.125	5.9e-11	1.95e-13	.361
Pd4h	2	1	.119	7.9e-12	0.78e-13	.318
Cu1e	2	2	.135	1.4e-11	0.75e-13	.406
Cu1f	4	2	.122	2.6e-11	2.27e-13	.389
Ni1c	2	2	.247	6.9e-9	4.76e-13	1.06
Ni1d	4	2	.252	4.6e-9	2.65e-13	-----

Arrhenius plot comparing He diffusivities



- Uncertainty: shift is due to normalization
- Release from traps obscures end of diffusive spectrum.
- Correct by stopping ramp before release from trap.

Summary

An experimental technique is being developed that appears capable of measuring He diffusivities in metals.

- 10^{10} to 10^{11} He atoms are implanted by a short, few keV He ion pulse at low temperature
- The sample chamber is quickly evacuated, then opened to a getter-pumped gas analyzer, with some additional He pumping for fidelity of the He desorption behavior
- The sample temperature is rapidly ramped to 400 K, producing
  (i) interstitial He diffusion from the sample and
  (ii) escape of He from trapping sites at higher temperatures.
- The desorption spectrum is analyzed with a linear expression describing Fickian diffusion, under short time and $E_D/kT > 10$ approximations.
  - The analysis gives both D_0 and E_D.
- He diffusion in Cu, Ni, and Pd is found to be around 10^{-13} cm^2/s at room temperature, but He trapping differs significantly.

Next Steps

- Reduce uncertainties
  - Energy (background correction)
  - Normalization (stop ramp)
- Lower implant temperature
- Vary implant fluence (clustering, trapping)
- Examine diffusivity in other materials
  - NG, fusion, alloys