Determination of hydrogen in niobium by cold neutron prompt gamma-ray activation analysis and neutron incoherent scattering

National Institute of Standards and Technology
Intro

• small interstitial hydrogen atoms cause “vacancies” in Nb crystal which lead to embrittlement and diminish superconducting abilities in Nb

• Two techniques for measuring H:
  
  • cold n prompt $\gamma$ activation analysis (PGAA) - $(n, \gamma)$ process - non-destructive, chemical form/shape not important, matrix independent, entire sample analyzed, fast, simultaneous for different isotopes
  
  • n incoherent scattering (NIS) - incoherent scattering cross section of hydrogen $>>$ absorption cross section - higher sensitivity and faster detection of H than PGAA - but signal is not specific to H, hence a H-less sample is needed to account for n scattering by other elements
Questions to Answer

• Does the acid treatment of the niobium introduce a measurable amount of hydrogen?

• Can vacuum heating remove hydrogen?
Neutron and Material

scattering vector: \( \vec{Q} = \vec{k}_f - \vec{k}_i \)

\[ \psi_i = e^{-ikz} \quad \psi_f = -\frac{b}{r} e^{-ikr} \]

\[ \frac{d\sigma}{d\Omega} = \frac{(\bar{b})^2}{N} \left| \sum_i N e^{i\vec{Q} \cdot \vec{r}} \right|^2 + (\bar{b}^2 - (\bar{b})^2) \]
Niobium

- $^{41}$Nb, atomic weight = 92.906
- soft, easily shaped
- low thermal neutron capture cross section
- At 1 atm, Nb has the highest critical temperature of the elemental superconductors, 9.3 K
- remains a superconductor even when inside high B field
Niobium

- treated with acid to remove surface impurities
- operating temperatures $2 \text{ K} \leq T \leq 4.2 \text{ K}$
- drop in superconductor’s $Q$-value observed at $75 \text{ K} \leq T \leq 130 \text{ K}$; attributed to hydride precipitation

$Q$ (quality) factor

$= \frac{\text{reactance}}{\text{resistance}}$

$= \frac{\text{stored energy}}{\text{energy loss rate}}$
NIST Cold Neutron Research Guide Hall

http://www.ncnr.nist.gov/instruments/coldinstr.html
neutron is captured, photon is promptly emitted with energy related to binding energy of added neutron.

\[ \gamma \text{ energies ID element species} \]
\[ \gamma \text{ intensities gives concentrations} \]
Fig. 1: cold neutron PGAA spectrometer

(bismuth germanate)

PGAA
• aircraft industry:
  • hydrogen embrittlement of titanium alloy jet engine turbine blades
  • hydrogen mass fraction of hydrogen-doped titanium alloy standard reference material
• hydrogen in semiconductors and related materials (quartz, germanium, thin films on silicon wafers)
• hydrogen in fullerenes
• PGAA + small angle neutron scattering (SANS) is used to study hydrogen impurity and pore size in nanocrystalline metals
SANS

- measure large objects (1-10³ μm)

SANS: http://www.ncnr.nist.gov/programs/sans/
Fig. 2: NIS measurement setup. Calibration using polypropylene films are done with this same setup.

information required:
(1) scattered neutron signal from sample
(2) blank measurement
(3) calibration of neutron signal vs. hydrogen concentration

each sample measured for 6 mins
Method

• 5 slabs of ultra-pure niobium, each ~ 10 g
• degassed at Jefferson Lab by heating in hot vacuum furnace (for ~ 6 h) to remove hydrogen
Jefferson Lab’s vacuum furnace

designed to operate at $10^{-8}$ torr

extending from the top of each niobium insert are a series of notches which are bent over to separate inserts together.
Results

both spectra show a peak at 2223 keV; similar magnitudes

Fig. 3: PGAA spectrum (H energy region) of Nb sample 4 after 1st vacuum heating (top), and then after acid treatment (bottom).
Fig. 4: Top: PGAA spectrum (H energy region) of Nb sample 4 after the 2nd vacuum heating. Bottom: PGAA spectrum of Nb sample 5 after 2nd degassing and 2nd acid treatment.

smaller 2223 keV peak

large 2223 keV peak
Fig. 5: The change in H concentration in Nb samples #4 (left) and #5 (right) relative to that after the 1st degassing as determined by PGAA. The results obtained after the 1st H loading are expressed as the “upper limit”, since the changes observed are within the measurement uncertainty. The significant changes occurred only after the 2nd degassing for #4, and 2nd H loading for #5. PGAA uncertainties are 2s based on propagation of counting statistics and uncertainties in element sensitivities, NIS uncertainties are 2s based on the propagation of uncertainty in the polypropylene film thickness.
Conclusion

• amount of H did not show correlation with time or temperature of initial degassing

• H content was not correlated with duration of initial acid treatment

• significant gain of H in sample 5 (after 2nd vacuum heating and 2nd acid treatment)

• 800 celsius heat removed strongly bound hydrogen, activating sites where H can be picked up by Nb upon subsequent acid treatment
Answers

1. Does acid treatment of Nb introduce a measurable amount of H?

2. Can vacuum heating remove H?

• answers:
  • NO for 1<sup>st</sup> cycle of treatment
  • YES for 2<sup>nd</sup> cycle
Resources

• http://www.ncnr.nist.gov/
• http://www.mrl.ucsb.edu/~pynn
• http://www.ansto.gov.au/ansto/bragg/