Determination of Hydrogen in Niobium by Cold Neutron Prompt Gamma-Ray Activation Analysis and Neutron Incoherent Scattering

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Abstract. The presence of trace amounts of hydrogen in niobium is believed to have a detrimental effect on the mechanical and superconducting properties. Unfortunately, few techniques are capable of measuring hydrogen at these levels. We have developed two techniques for measuring hydrogen in materials. Cold neutron prompt gamma-ray activation analysis (PGAA) has proven useful for the determination of hydrogen and other elements in a wide variety of materials. Neutron incoherent scattering (NIS), a complementary tool to PGAA, has been used to measure trace hydrogen in titanium. Both techniques were used to study the effects of vacuum heating and chemical polishing on the hydrogen content of superconducting niobium.

INTRODUCTION

The presence of even trace amounts of hydrogen is known to alter the properties of many materials. Hydrogen is known to cause embrittlement in metals and to change the electrical properties of semiconductor materials. NIST recently began a collaboration with Jefferson Laboratory to study hydrogen in niobium metal. Jefferson Laboratory is responsible for building the accelerator that is the heart of the Spallation Neutron Source. The high-purity niobium used to build the superconducting resonant cavities must be chemically polished (treated with acid) to remove surface imperfections which could alter the superconducting properties. This chemical polishing is believed to introduce trace hydrogen, which may be detrimental to mechanical and superconducting properties as the niobium is cooled to operating temperatures of $2\text{ K} \leq T \leq 4.2\text{ K}$.¹ A significant drop in the superconductor's Q-value has been observed at $75\text{ K} \leq T \leq 130\text{ K}$, and has been attributed to hydride precipitation of interstitial hydrogen.¹ Unfortunately, definitive studies of this phenomenon have been hampered by a lack of techniques yielding reliable quantitative measurement of hydrogen below 100 mg/kg.

At NIST, we have developed two techniques for the measurement of hydrogen in materials. In the first technique, prompt gamma-ray activation analysis (PGAA), the sample is irradiated with a beam of neutrons, inducing elemental nuclei to undergo neutron capture and emit prompt gamma rays upon de-excitation. The gamma rays are then measured using a high-resolution germanium detector.

Comparison with standards yields quantitative multielemental analysis. The measurement is nondestructive, chemically specific, matrix independent, and because both neutrons and gamma rays are penetrating, the entire sample is analyzed. Furthermore, because the measurement arises from a nuclear reaction, the results are independent of the chemical form of the element being determined. The presence of hydrogen is indicated by the appearance of a 2223 keV gamma-ray.

The second technique developed for measuring hydrogen is neutron incoherent scattering (NIS). NIS takes advantage of the anomalously high incoherent scattering cross section for hydrogen ($\sigma_{\text{bound}} = 80 \text{ b}$). The sample is placed in a neutron beam, and neutrons scattered from the sample are measured using a ^3He detector. Because the neutron scattering cross section for hydrogen is much larger than the absorption cross section ($\sigma_{\gamma} = 0.3 \text{ b}$), the NIS technique achieves a higher sensitivity and more rapid detection of hydrogen than PGAA. The disadvantage is that the signal is not specific to hydrogen, hence a reliable blank (same matrix as the sample but containing no hydrogen) is needed to account for neutron scattering by other elements. Nevertheless, we have found NIS to be a useful complementary tool to PGAA for hydrogen measurement.

In the sections that follow we describe the experimental setup for each technique and list past applications. We then relate how the two methods were used to study hydrogen in niobium.

TECHNIQUE

Prompt Gamma-ray Activation Analysis

The PGAA spectrometer, located in the cold neutron guide hall of the NIST Center for Neutron Research,²⁻⁵ is depicted in Figure 1. Neutrons from the reactor core pass through a liquid hydrogen cold source to lower their kinetic energy and are then transmitted through a ^{58}Ni coated guide to the PGAA station. The use of cold neutrons and guides results in better sensitivity and lower background than achievable with most thermal neutron PGAA instruments. The neutron beam is collimated by a 2 cm aperture in a piece of ^6Li enriched glass before striking the sample. Prompt gamma rays emitted from the sample are measured by a lead and cadmium shielded high-resolution germanium detector. The detector is surrounded by a bismuth germanate Compton suppressor, which reduces the spectrum baseline (improving signal-to-noise ratio) by suppressing counts arising from scattered gamma rays. The signal is processed using appropriate electronics⁴, and gamma-ray spectra up to 10 MeV are displayed using a computer workstation. Samples may be irradiated in an evacuated sample chamber to reduce hydrogen background due to atmospheric water vapor. The hydrogen background measured from the irradiation of the empty evacuated sample chamber is $0.05 \text{ counts}\cdot\text{s}^{-1}$, equivalent to $3 \mu\text{g}$ of hydrogen measured at the sample position. In the absence of spectral interferences, the detection limit for hydrogen in many materials is $< 10 \text{ mg/kg}$.

Figure 1. Cold neutron PGAA spectrometer at the NIST Center for Neutron Research

The cold neutron PGAA instrument has been used to measure hydrogen and other elements in a wide variety of materials. Because the presence of hydrogen can alter material properties, much work has been devoted to the measurement of hydrogen impurity in materials. PGAA has been used to study hydrogen embrittlement of titanium alloy jet engine turbine blades^{6, 7} and to certify the hydrogen mass fraction of a hydrogen-doped titanium alloy standard reference material produced for the aircraft industry.⁸ A combination of PGAA and small angle neutron scattering (SANS) has been used to study hydrogen impurity and pore size in nanocrystalline metals.⁹ PGAA has also been used to measure hydrogen in semiconductors and related materials, including quartz¹⁰, germanium¹⁰, and thin films on silicon wafers. PGAA has been used to measure hydrogen impurity in fullerenes¹¹ and other materials to determine their suitability for use in neutron scattering studies. Neutron scattering techniques yield valuable information on the structure of such materials, however, the presence of hydrogen in the sample introduces a large incoherent scattering background into the measurements, which may be corrected only if the hydrogen content is known. PGAA has also been used to study hydrogen uptake by solid proton conductors^{12, 13} that have potential for use in fuel cells and to study moisture content as a function of position in concrete¹⁴. In an ongoing investigation PGAA is being used to characterize the stoichiometries of fluorocarbon thin films, which have potential for use as membranes in fuel cells. Measurement of the H/S ratios in the films has yielded vital information needed to improve the synthesis of these materials.¹⁵

Neutron Incoherent Scattering

The experimental setup for NIS is schematically shown in Figure 2. The sample is placed in a Cd lined chamber, with a 9-mm Cd aperture defining the incident beam, which has passed through a Be filter removing neutrons below 4 Å. A ^3He detector is placed 45° from the direction of the incident beam, viewing the sample through a Cd sleeve. A second ^3He detector may also be placed at a different angle in addition to the first detector in order to measure neutrons scattered in the backward direction, as the incoherent scattering for hydrogen may not be isotropic in some systems.^{16,17} However, for a particular system with a specific calibration, one detector will suffice, provided a linear relationship can be established between the scattered neutron intensity and the amount of hydrogen.

Determination of hydrogen concentration by NIS requires three pieces of information: (1) the scattered neutron signal from each sample, (2) a blank measurement to account for neutrons scattered by other elements in the sample, and (3) a calibration curve giving neutron scattering signal as a function of hydrogen concentration. In the absence of a blank, a relative change in the amount of hydrogen in the sample may still be determined if the change is assumed to be due to hydrogen only. As an example, NIS was used to analyze samples of titanium alloy containing from 100 to 300 mg/kg hydrogen.¹⁶⁻¹⁸ A titanium alloy disk of the same size as the samples, degassed by vacuum heating at 800 °C for 20 h, was measured as a blank. Hydrogen content was calibrated as a function of scattering signal by placing polypropylene films of known hydrogen mass fraction in front of the titanium alloy and measuring the scattered neutrons after the addition of each film. Hydrogen mass fractions determined in this manner by NIS were in agreement with those measured by PGAA.

Fig. 2. Schematic drawing for the NIS measurement setup. The calibration using polypropylene films have been carried out using the same setup.

EXPERIMENT

In this investigation we set out to answer two questions: Does the acid treatment of the niobium introduce a measurable amount of hydrogen into the material, and can the hydrogen be removed by vacuum heating? In order to answer these questions, we made measurements on five rectangular slabs of ultrapure niobium, each weighing approximately 10 g. Prior to acid treatment, the niobium samples were degassed at Jefferson Laboratory by heating in a high temperature vacuum furnace in order to attempt to remove as much hydrogen as possible. The temperature and duration of this heating for each sample is given in Table 1, column 1. Measurements made on the degassed samples were meant to serve as a baseline for comparison with measurements made after acid treatment.

The degassed samples were sent to NIST for measurement of hydrogen by cold neutron PGAA. Each sample was irradiated for at least 6 hours with a 1 cm collimated neutron beam inside an evacuated sample chamber. Thin disks of niobium foil and urea (containing 6.67 wt. % hydrogen) were irradiated as standards. A background spectrum then taken of the empty sample holder similarly irradiated. In each spectrum the hydrogen peak at 2223 keV and the niobium peak at 5104 keV were analyzed. A hydrogen background count rate of $0.05 \text{ counts}\cdot\text{s}^{-1}$ was subtracted from each sample count rate to give the background corrected count rate. Hydrogen and niobium sensitivities ($\text{counts}\cdot\text{s}^{-1}\cdot\text{mg}^{-1}$) were determined from the irradiation of the standards. Milligrams of hydrogen and niobium were calculated by dividing sample count rate by sensitivity. These values were converted to atoms of H and Nb, and then to % atom fraction of hydrogen.

After the baseline measurements were completed, the samples were sent back to Jefferson Laboratory for chemical polishing. Samples were polished by subjection to acid treatment, with voltage applied in an attempt to load hydrogen. The duration of the treatment for each sample is given in Table 1, column 3. The samples were returned to NIST where a second hydrogen determination was performed on each piece. The procedure used was identical to that described above.

The acid treated samples were also analyzed by NIS, using the same setup as shown in Figure 2. Each sample was measured for 360 seconds, with counting statistics of better than 1%. A background run (empty aperture) was also performed, and the background count rate subtracted from each sample count rate to obtain the net scattered intensity from each sample. The count rate was calibrated as a function of hydrogen content using the polypropylene films addition method described earlier. Each layer of polypropylene film used with the Nb bulk sample represented $(21.1 \pm 2.0) \text{ mg/kg}$ of H in Nb, or $(0.194 \pm 0.018) \%$ atom fraction of hydrogen (uncertainties are 1s). The uncertainty was estimated based on the propagation of uncertainty in the polypropylene film thickness ($5.5 \mu\text{m} \pm 0.5 \mu\text{m}$, with 1s uncertainty), which dominates over the counting statistics.

Because the samples were not measured by NIS before acid treatment, there was no baseline against which to compare the measurements. Therefore, niobium

Table 1. Treatment of niobium samples measured in this investigation.

Sample	Measurement 1 following:	Measurement 2 following:	Measurement 3 following:	
	Vacuum heating 1	Acid treatment 1 duration (min)	Vacuum heating 2	Acid treatment 2 duration (min)
Nb 2	800 °C / 6 h	1	---	---
Nb 3	700 °C / 6 h	2	---	---
Nb 4	750 °C / 6 h	3	800 °C / 6 h	---
Nb 5	600 °C / 6 h	0.5	800 °C / 6 h	5
Nb 6	Not heated	4	---	---

samples 4 and 5 were returned to Jefferson Laboratory and subjected to a second vacuum heating for 6 hours at 800 °C, in order to remove the hydrogen. Sample 5 was then again subjected to hydrogen loading via acid treatment with applied voltage. Both samples were returned to NIST and again measured by both NIS and PGAA, in order to discern whether the hydrogen content of the two samples differed.

RESULTS AND DISCUSSION

While the relative change in the amount of hydrogen in the samples before and after each treatment can be easily determined by both PGAA and NIS, the absolute amount of hydrogen at any stage is not well defined. The principle difficulty in the determination of the absolute amount of hydrogen by either technique is the lack of a true blank. Such a blank is necessary for NIS, because neutrons scattered from the sample by hydrogen cannot be distinguished from neutrons scattered by niobium or other elements in the sample. For measurement of hydrogen at very low levels by PGAA, a blank may also be necessary due to the possibility of spectral interferences. Although current prompt gamma-ray compilations do not list a niobium peak at 2223 keV that would interfere with hydrogen measurement, it is unlikely that all prompt gamma-rays lines in the niobium spectrum have been catalogued. Due to the high density of neutron capture levels for many elements, PGAA spectra often consist of thousands of peaks, the tiniest of which are not listed in prompt gamma-ray compilations. Figure 3 shows the spectrum of Nb sample 4 after the first vacuum heating, and again after acid treatment. Both spectra show a peak at 2223 keV, which, if due to hydrogen, yields the equivalent of ~ 0.3 % atom fraction of hydrogen. However, without a well defined niobium blank (known to contain no hydrogen), it is difficult to determine whether this peak is indeed entirely due to hydrogen, or whether there is an underlying niobium interference peak at this same energy. Furthermore, since a peak at 2223 keV in excess of the hydrogen background count rate was observed in

Figure 3. PGAA spectrum (H energy region) of Nb sample 4 after first vacuum heating (top), and then after acid treatment (bottom).

Figure 4. Top: PGAA spectrum (H energy region) of Nb sample 4 after the second vacuum heating. Bottom: PGAA spectrum of Nb sample 5 after second degassing and second acid treatment.

every PGAA spectrum taken of these samples, it is impossible to say that any of the samples achieved zero hydrogen content after vacuum heating.

Figure 4 shows the PGAA spectrum of Nb sample 4 taken after the second vacuum heating. This spectrum shows a much smaller signal at 2223 keV than previously observed for this sample, indicating that significantly more hydrogen was removed than in the first vacuum heating. Since this measurement yielded the lowest hydrogen signal for both PGAA and NIS, it was decided to use the twice degassed

sample of Nb 4 as a blank (zero hydrogen by definition) and express all measurements relative to the signal given by the blank.

Table 2 shows hydrogen fractions in the niobium samples calculated relative to the blank. For most measurements, hydrogen fractions determined by PGAA are in agreement with those determined by NIS. For four of the five samples, no measurable hydrogen gain was noted between the first vacuum heating and the first acid treatment. The PGAA measurements indicated an increase in the hydrogen content of sample 2 after acid treatment, however this increase was not confirmed by the NIS measurements. However, both techniques measured a significant increase in hydrogen content for sample 5 after the second acid treatment (see Figure 4).

Table 3 shows the gain or loss in hydrogen fraction for each sample after each processing. Columns 2 and 3 represent the gain in hydrogen fraction (relative to the initial hydrogen fraction measured in the first set of baseline PGAA measurements) measured by PGAA and NIS after the first acid treatment. For the samples that showed no measurable gain, this H gain is expressed as an upper limit, determined by subtracting the PGAA baseline measurements from the PGAA and NIS measurements after acid treatment. As stated above, the PGAA measurements indicated an increase in H fraction for sample 2 after acid treatment, but the NIS measurement does not confirm this. However, both techniques did measure a

Table 2. Hydrogen fractions measured in the niobium samples. Samples were measured after vacuum heating (#1) and again after acid treatment (#2). Samples 4 and 5 were measured again (#3) after a second vacuum heating (4 and 5) and acid treatment (5 only). All H fractions are measured relative to the twice degassed Nb 4 sample (measurement #3), which was taken as a blank. 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.

Sample	% atom fraction hydrogen (determined relative to Nb 4 measurement #3)				
	#1	#2		#3	
	PGAA	PGAA	NIS	PGAA	NIS
Nb 2	0.138 ± 0.025	0.257 ± 0.041	0.153 ± 0.032	---	---
Nb 3	0.156 ± 0.026	0.169 ± 0.028	0.167 ± 0.034	---	---
Nb 4	0.122 ± 0.028	0.114 ± 0.027	0.083 ± 0.020	"0"	"0"
Nb 5	0.107 ± 0.025	0.107 ± 0.025	0.113 ± 0.024	0.396 ± 0.037	0.352 ± 0.070
Nb 6	0.126 ± 0.027	0.140 ± 0.028	0.150 ± 0.032	---	---

Table 3. Hydrogen gain measured in niobium samples measured by PGAA and NIS. Gains are measured relative to the first PGAA measurements made after vacuum heating. 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. Upper limits were calculated based on 2s uncertainties.

Sample	Change in H concentration (% atom fraction hydrogen)					
	After 1 st acid treatment		After 2 nd vacuum heating		After 2 nd acid treatment	
	PGAA	NIS	PGAA	NIS	PGAA	NIS
Nb 2	0.110 ± 0.040	≤ 0.04	---	---	---	---
Nb 3	≤ 0.05	≤ 0.04	---	---	---	---
Nb 4	≤ 0.03	≤ 0.01	- 0.110 ± 0.028	- 0.083 ± 0.018	---	---
Nb 5	≤ 0.03	≤ 0.03	not measured	not measured	0.277 ± 0.046	0.240 ± 0.048
Nb 6	≤ 0.05	≤ 0.05	---	---	---	---

significant decrease in H fraction for sample 4 (relative to the previous measurements) after the second vacuum heating and a significant increase in H fraction for sample 5 after the second acid treatment. This result is again depicted in Figure 5, where the results obtained after the 1st H loading are expressed as the “upper limit”, since the changes observed are within the measurement uncertainty.

In conclusion, the amount of hydrogen measured in the niobium samples after the initial vacuum heating did not show any correlation with the time or temperature of degassing, nor did hydrogen content after the initial acid treatment correlate with duration of the treatment. However, the results obtained for samples 4 and 5 after the second vacuum heating and acid treatment respectively indicate that both processes can affect the hydrogen content of the niobium. Therefore, the answers to the two questions we set out to ask are “no” for the first cycle of treatment but “yes” for the second cycle. One possible explanation for the significant gain in hydrogen by sample 5 is that heat treatment at 800 °C causes removal of strongly bound hydrogen, thereby activating sites where hydrogen can be picked up by the niobium upon subsequent acid treatment. The removal of this strongly bonded hydrogen during the heat treatment may also be responsible for the observed changes in the mechanical properties of the niobium.¹ Additional measurements are necessary in order to fully understand these processes.

In the future, it may be feasible to study the nature of the hydrogen bonding in the samples by NIS. The current NIS measurements were carried out at room temperature. In theory the nature of the hydrogen bonding can be distinguished by measuring the scattering cross section as a function of H concentration.¹⁹ Likewise, dependence of other factors such as temperature should give the same information. Between a free atom and a rigidly bound atom, the hydrogen can behave like a

lattice gas or like an anisotropic harmonic oscillator. At temperatures sufficiently low where H in Nb precipitates, the temperature dependence of the scattering cross section can be a tell-tale indicator of these behaviors. Preliminary NIS experiments on H-Ti systems cooled to liquid nitrogen temperature and warmed freely to room temperature, with data collected every 30 s, indicated differences in temperature dependence of the scattered intensity for the three different H concentrations.²⁰ There are dedicated neutron scattering instruments (inelastic and quasi-elastic scattering) to study the nature of the hydrogen bonds, but at these low concentration levels the measurements are difficult. The total scattering technique we employed has the advantage of rapid data collection even with these sample sizes and concentrations. For future experiments, we plan to conduct temperature dependent NIS measurements on H in Nb to investigate the H precipitation process.

Fig. 5. The change of 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.

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