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SANS Measurement of Hydrides in Uranium

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Abstract

SANS scattering is shown to be an effective method for detecting the presence of hydrogen precipitates in uranium. High purity polycrystalline samples of depleted uranium were given several hydriding treatments which included extended exposures to hydrogen gas at two different pressures at 630°C as well as a furnace anneal at 850°C followed by slow cooling in the near absence hydrogen gas. All samples exhibited neutron scattering that was in proportion to the expected levels of hydrogen content. While the scattering signal was strong, the shape of the scattering curve indicated that the scattering objects were large sized objects. Only by use of a very high angular resolution SANS technique was it possible to make estimates of the major diameter of the scattering objects. This analysis permits an estimate of the volume fraction and means size of the hydride precipitates in uranium.

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Introduction

The effect of hydrogen on the properties of uranium and uranium alloys through precipitate formation is well known (1). Characterization of hydrogen and hydrides in uranium is essentially impossible below a certain size scale with conventional techniques. Neutron scattering offers a unique method of characterizing hydrogen species in uranium through the special nuclear scattering properties of hydrogen and uranium. The nuclear scattering amplitude describes the neutron scattering strength. For hydrogen the scattering amplitude is -0.374×10^{-12} cm and for uranium is 0.841×10^{-12} cm (2). Note the difference in sign. This particular combination of scattering amplitudes can be used to great advantage in small angle neutron scattering where the scattering contrast between a uranium matrix and a UH_3 hydride precipitate is very favorable for scattering measurements. Small angle scattering provides a variety of statistical measures of nonperiodic structures such as clusters and precipitates(3,4). In the simplest applications, a scattering sample is modeled by a set of scattering objects. These objects are defined in terms of their scattering density that is given by the local scattering amplitude per volume. When the scattering centers are distributed randomly in space, the diffraction pattern from each center is added to give a net scattering. The form of the resulting diffraction pattern depends on the distribution of sizes and shapes for the set of scattering centers. For example, in the limit of very small angle scattering, one generally observes a scattering in the form of a Gaussian curve. Analysis of this form yields an average radius of the particles. At large angles of scattering, in the case where a distinct boundary exists between the precipitate and the matrix, the intensity falls off as the fourth power of the scattering angle and the multiplier of the power law is proportional to the interfacial area per volume of the sample. The interpretation of small angle scattering data should ideally be supported by microscopic examination of the scattering sample if at all possible. Because electron microscopic examination of hydride containing uranium has proven to be very difficult, our use of small angle scattering makes limited use of structural modeling for this presentation.

Preparation of Uranium Metal Specimens for SANS Examination

Two types of uranium metal stock were used to prepare the specimens. One type ("clean") was unalloyed metal as reduced from highly purified uranium tetrafluoride using magnesium metal. This is the most pure form commonly available. The second type ("dirty") was also "unalloyed", but had been processed in a way that incorporated significant contaminants in the matrix. Partial chemical analyses of these two materials are shown in Table 1. The numbers are as-reported by the laboratory and are probably individually accurate to better than a factor of 2. This listing represents most of the total contamination, and essentially all of the contamination that is expected to result in precipitation of second phases on cooling of the matrix. For the "clean" material, a listing of the complete chemical analysis can be found in a previous publication (5). The hydrogen levels given in this table are for illustrative purposes only; for each material type, samples with a range of H content were prepared. The total non-uranium entry includes elements not listed in this abbreviated table. Also given in the table are estimates of the volume fraction taken up by the principal resultant precipitating phases. The volume fractions are calculated from elemental atomic weight and equilibrium binary solubility data(6), phase stoichiometry, and phase density. Thus, the "clean" uranium (with zero ppm H) is expected to have 0.23% of its volume occupied by inclusions, and the "dirty" uranium (with 14.74 ppm H) is expected to have 3.96% inclusion volume. The starting material for the specimens was uranium rod, 12.7 mm diameter by 150 mm long machined from cast material. The rods were exposed to known pressures of ultra-pure hydrogen gas (99.9999% purity, filtered through a UH_3 powder bed), at known temperatures, in a fused quartz tube (5). On completion of the exposure cycle, the sample stock rods were either slow-cooled, or quenched by fracturing the tube and allowing the rod to fall into water.

Quartz capsules were made by joining a parallel sided spectroscopy cuvette with dimensions of 5mm by 10mm cross section and 40 mm length to a ground glass seal and cap that provided a convenient sample containment and mount for small angle scattering measurements. The uranium samples were machined into 12.7 mm diameter rods and cut into disks 4.5 mm thick. The sides of the disks were machined to a width of 9.5 mm to fit into the quartz capsule.

Table 1 – Expectations of Inclusion Population for “Clean” and “Dirty” Uranium Metal

Elemental Contaminant	Level (wtppm)		Precipitating Phase	Precipitate Volume Fraction	
	“Clean”	“Dirty”		“Clean”	“Dirty”
H	0.0	14.74	UH ₃	0.0000000	0.002015
B	0.06	0.10	UB ₂	0.0000011	0.0000018
C	19	332	UC	0.00055	0.00948
N	17	15	UN	0.00035	0.00030
O	18	25	UO ₂	0.00016	0.00026
Al	10	50	UA ₂	0.00012	0.00060
Si	10	600	U ₃ Si	0.00032	0.01901
P	1.2	50	UP	0.0000000	0.000000
S	0.2	5	US	0.0000000	0.000000
Mn	7.7	60	U ₆ Mn	0.000223	0.00171
Fe	12	175	U ₆ Fe	0.00034	0.0049
Ni	5	40	U ₆ Ni	0.000137	0.0010
Cu	2	40	UCu ₅	0.000006	0.00012
Zn	5	5	U ₂ Zn ₁₇	0.000016	0.000016
As	0.06	5	UAs	0.0000000	0.000000
W	0.03	50	W	0.0000000	0.000048
<i>Subtotal</i>	107	1466			
<i>Total non-U</i>	134	1554	<i>Total Misc.</i>	0.0022	0.040

The disks were heated in vacuum and cooled or charged with hydrogen according to the following preparations. In the Slow Cooled preparation the sample was heated in vacuum for 12 hrs at 630°C and furnace cooled to room temperature. In the Water Quenched condition the sample was heated in vacuum for 2 hrs at 850°C and water quenched. In the Low Hydrogen condition the sample was heated in vacuum for 1 hour at 850°C, exposed to hydrogen at 8.2 Torr for 1 hr at 850°C, and water quenched. Finally, in the High Hydrogen condition the sample was heated in vacuum for 1 hr at 850°C, exposed to hydrogen at 701 Torr for 1 hr at 850°C hydrogen, and water quenched.

The neutron scattering contrast for the hydride in uranium is based on the assumption that the hydride has the composition of UH₃. The cubic UH₃ unit cell lattice parameter is 4.161 Å and the unit cell contains 2 hydride molecules. The structure of the uranium matrix is orthorhombic with a density of 19.05 gm/cc. From these parameters the scattering amplitude per volume is $-0.78 \cdot 10^{10} \text{ cm}^{-2}$ for the hydride and $4.05 \cdot 10^{10} \text{ cm}^{-2}$ for uranium. The scattering amplitude difference is $4.83 \cdot 10^{10} \text{ cm}^{-2}$. The scattering contrast is a bit larger than the contrast factor for a void in uranium metal matrix.

The 8-m SANS instrument at NIST is a moderate resolution instrument suitable for examining structural features in materials from roughly 1 to 100 nm. Following the liquid-nitrogen cooled filter, a mechanical velocity selector is used to tune the wavelength from 5 to 20 Å. The instrument has a computer-controlled translation stage that accommodates multi-specimen sample changers. The detector is a 64 cm x 64 cm position-sensitive proportional. Counts from the detector accumulate in histogramming memory.

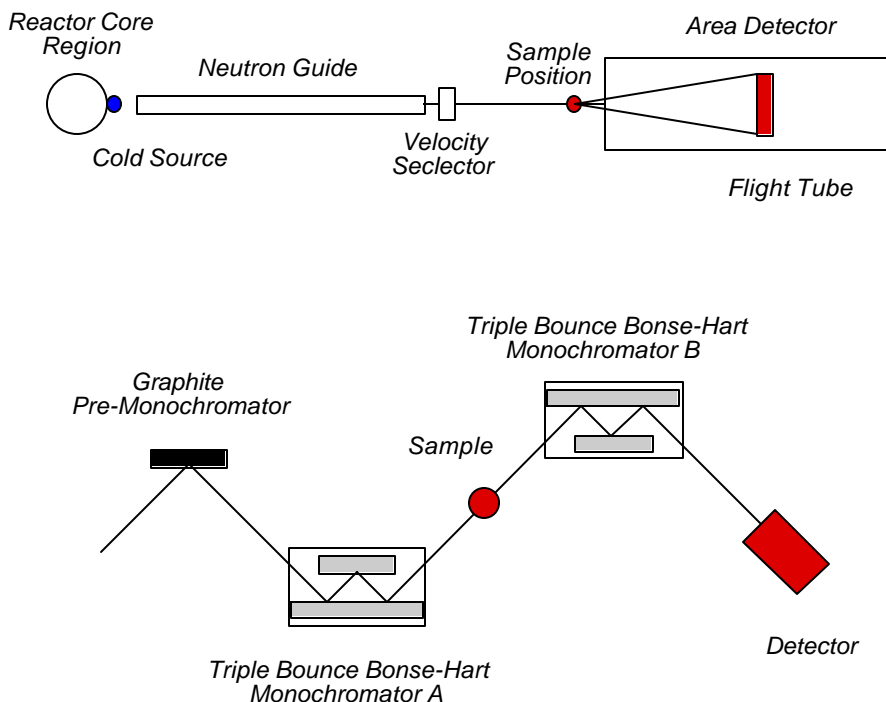


Figure 1. Schematic diagrams of the small angle scattering apparatus at NIST. Top, conventional SANS applicable to the 8-meter and 30-meter machines. Bottom, USANS

NG-3 30-meter small angle neutron scattering instrument is designed to cover a wide Q-range, from 0.015 to nearly 6 inverse nanometers, and is suitable for examining structural features in materials ranging from roughly 1 to 500 nm. Neutrons from the cold source pass through a mechanical velocity selector with variable speed and pitch, enabling both the mean wavelengths to be varied over a wide range. Circular pinhole irises in a 15-m long evacuated pre-sample flight path collimate the monochromatic beam. The sample is located on a computer-controlled translation stage. The 2-D position-sensitive detector (650 mm x 650 mm with 10 mm resolution) can be moved along the flight path to vary the sample-to-detector distance from 1.2 m to 13 m.

A perfect crystal diffractometer (PCD) for ultra-high resolution small-angle neutron scattering (USANS) measurement operates at the thermal neutron beam port, BT-5. The PCD increases the maximum size of features accessible with the 30-m SANS by nearly two orders of magnitude, from 10^2 nm to 10^4 nm. The PCD is a Bense-Hart-type instrument with large triple-bounce, channel-cut silicon (220) crystals as monochromator and analyzer. The perfect crystals provide high angular resolution while the multiple reflections suppress the “wings” of the beam profile, improving the signal-to-noise ratio to values comparable to that obtained with pinhole instruments.

The 8-meter instrument was used to measure the upper range of scattering angles with low angular resolution. The 30-meter instrument was used for intermediate angle measurements with higher resolution and the USANS instrument was used for very low angle and high resolution. The nominal wavelengths used were 8 Å and 12 Å respectively. The ultra SANS instrument uses a 2.5 Å neutron scattered from a silicon crystal monochromator. The geometry of the USANS achieves a very high resolution only in the scattering plane so that scattering is collected by the equivalent of a very narrow slit. The measured data requires a desmearing correction (7) to permit comparison of data between the conventional SANS instruments.

Data are corrected for sample transmission, background scattering and detector efficiency. Standard scatterers are used to calibrate the scattering in absolute scattering cross section units. In the 8-meter and 30-meter SANS instruments the data collected in the area position-sensitive

detectors are averaged to yield a scalar intensity versus Q curve. The scattering vector magnitude, Q, is given by $4\pi\sin\theta/\lambda$ where θ is half the scattering angle and λ is the wavelength. These data can be desmeared numerically by calculations exemplified by Lake(7). These correction procedures are very effective if undistorted scattering at large angles have been measured and can be used with the USANS data. The high angle data are artificially smeared and then added to the USANS data set. These data are then desmeared over the angular range of the original USANS data and then added to the data collected in the conventional instruments.

Results

Porod scattering appears to dominate scattering over the whole range of scattering measurements as shown in Figure 2. At smallest Q, scattering is dominated by the scattering coming from a small volume fraction of very large scattering objects. At larger Q's a second contribution, spread over a wide range of scattering vector, becomes the dominant scattering effect. This is taken to be the major hydride scattering effect. At high Q's the scattering is almost purely Porod-like but differences between the clean and dirty uranium samples are nevertheless apparent. The distinction between hydride scattering and scattering from vary large impurities was only made apparent in the very low Q USANS measurements. The data are reviewed chronologically starting with the high Q measurements taken in December 1998 and ending with the inclusion of USANS measurements taken in August 2000.

At low resolution the difference in the "clean" scattering between the water quenched sample and the slow-cooled sample is in the form of Guinier scattering. The Guinier radius extracted from this scattering is 104 Å. Chemical analysis suggests that this scattering would have to arise from a non-hydride captured during water quenching process. The data for the dirty uranium shows a general separation between the water quench and slow-cooled sample scattering. However, no scattering characteristic of a 100 Å precipitate could explain the difference in the curves. Further work on hydrogen-free uranium is needed to clarify these observations.

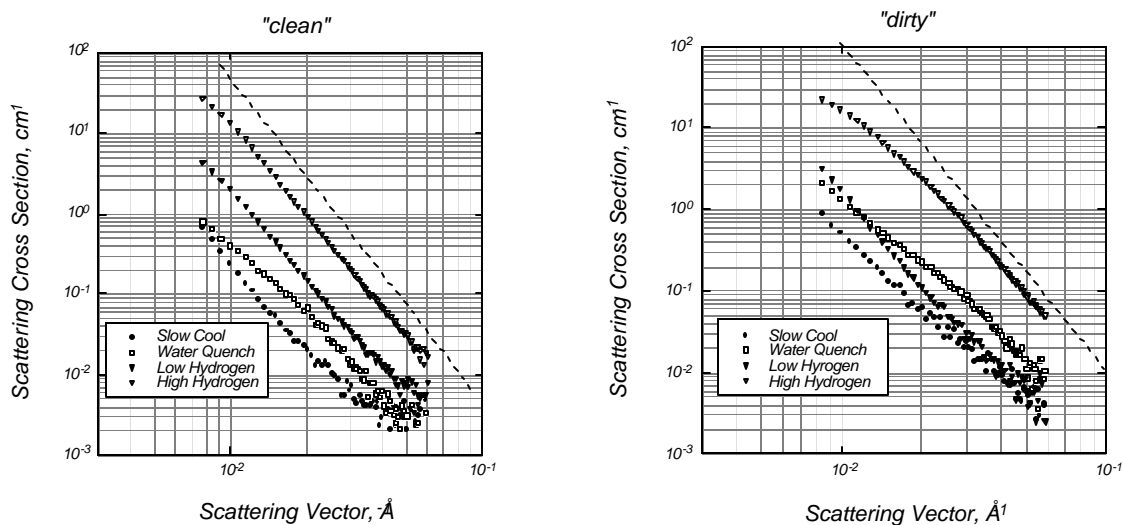


Figure 2 Low-resolution data for “clean” (left) uranium and “dirty” uranium (right). Note the dashed line for comparison with the Q^{-4} Porod law.

A nine-month interval separated the measurements of the “clean” and “dirty” uranium samples that permitted the examination of the stability of the samples. Data were collected for the "clean" uranium in the slow-cooled and water quenched condition at both the early and later experimental sessions. These data are shown in Figure 3. Scattering for the 1999 session is slightly, but noticeably, higher than scattering measured in 1998. The change might be attributed to an uptake of hydrogen from water vapor leaking through the ground glass seals on the quartz

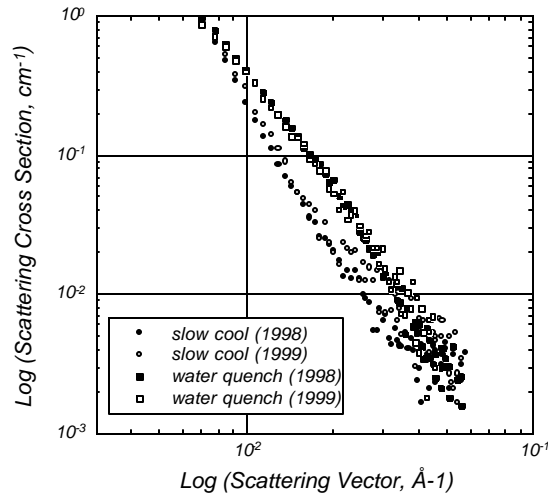


Figure 3. The effect of storage over a 9-month period.

capsules. The effect appears to be small. The scattering data for the high and low hydrogen conditions are found to match very well between the two experimental sessions.

Data taken at medium and high resolution combined with the low-resolution data are shown in Figure 4 and give a clearer indication of the differences in hydrogen uptake between the dirty and clean uranium. For “clean” uranium, the hydride scattering from the high hydrogen differs

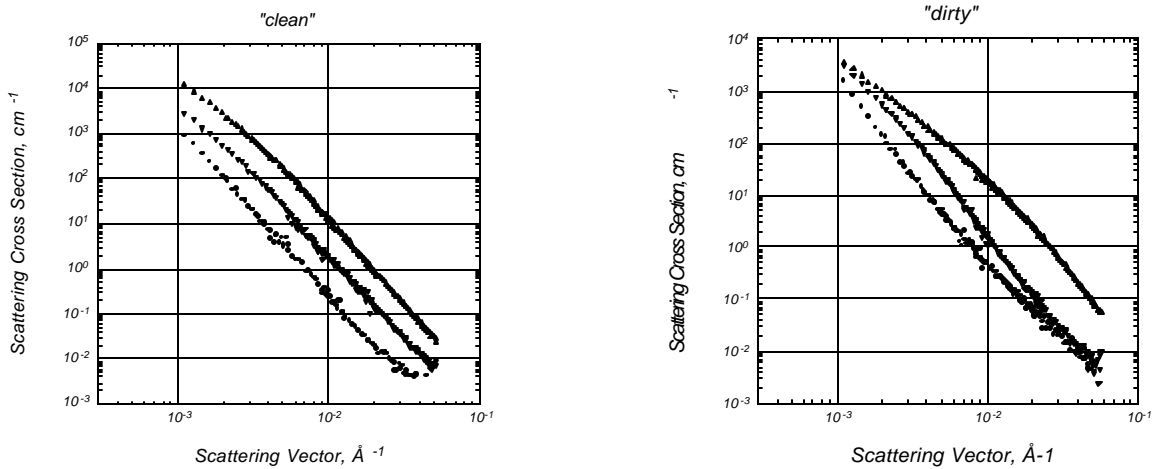


Figure 4. Conventional SANS data at low, medium and high resolution. (left) “Clean” (right) “Dirty”. Triangle symbol up High Hydrogen, triangle down, Low Hydrogen, circle Slow Cool.

from the scattering from the low hydrogen by a simple multiplicative factor. One can conclude that the principal difference between the hydride structures is number density alone. For the dirty uranium, the hydride structures differ in a more interesting way. In the high hydrogen case, morphology having a length scale similar to that in the clean uranium prevails. But for low

hydrogen, the characteristic scale is larger and so displaces the scattering to a smaller angle. It

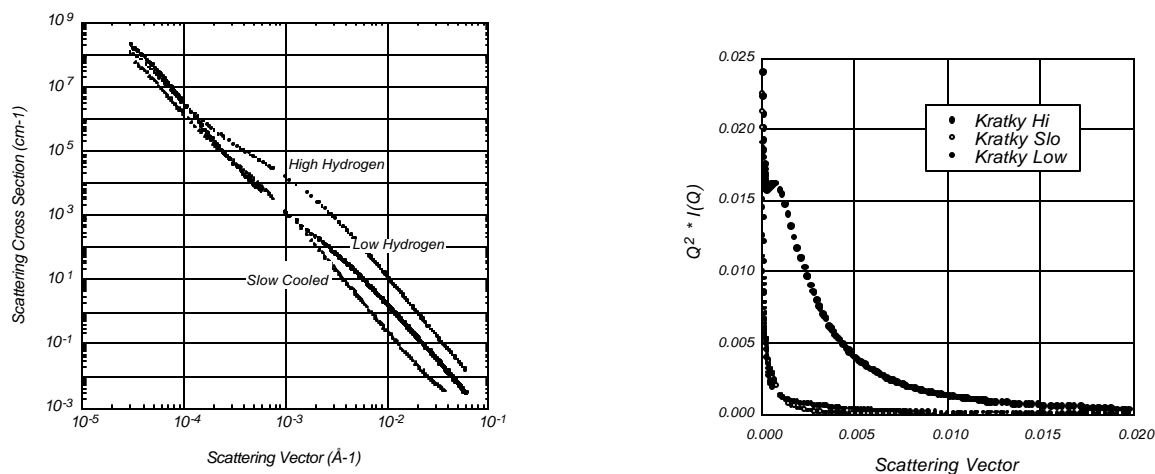


Figure 5. (a) Consolidated “Clean” data including USANS (desmeared), high resolution, medium resolution and low resolution. (b) The area under the Kratky plot (given by Q^2 times the scattering cross section) gives the so-called scattering invariant.

would appear, that for lower hydrogen loading in the dirty uranium, the hydrides are either not growth limited or the nucleation rate is lower.

Corrected USANS data for “clean” uranium is combined with the conventional SANS data in Figure 5a. The two dominating Porod scattering contributions are seen at low Q in the USANS data and at high Q in the 8-meter data. The USANS measurements reach into sufficiently small Q to cover a range of scattering that permits evaluation of the volume fraction of hydride. The Kratky plot given by Q^2 times the scattered intensity is shown in Figure 5b. The integration of these curves gives the so-called scattering invariant and is equal to the product of the volume fraction and the scattering contrast divided by 2π . The scattering invariant is calculated from the area over the observed range plus an extended integration over an assumed Porod behavior from large Q to “infinity”. The calculation gives a volume fraction of 0.140% and 0.070% for the high and low hydrogen respectively. The results are lower than would be calculated from the chemical analysis for hydrogen. However, the data used were smoothed from rather irregular intensity numbers from the tails of the USANS data as well as a significant gap between the USANS and SANS data. Under the circumstances, the fit is considered to be qualitatively acceptable, giving a reasonable ratio between the two hydrogen preparations albeit lower than anticipated.

The Guinier plot shown in Figure 6 is made from the desmeared USANS data for the High hydrogen, Low hydrogen and Slow Cooled conditions for “clean” uranium. The plot indicates the possibility that two Guinier radii may apply to the structure model, specifically plate-like objects with a diameter-to-thickness ratio of 10:1. The major axis is in the range of 2 to 10 micrometers

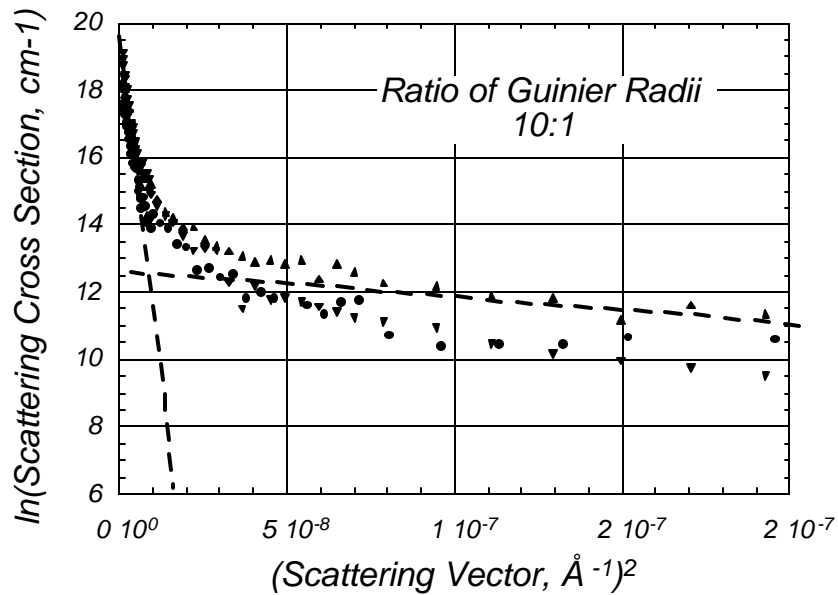


Figure 6. Guinier plot of small angle scattering from “clean” uranium. Triangle symbol up High Hydrogen, triangle down, Low Hydrogen, circle Slow Cool

Preliminary attempts to fit the scattering over the whole range of scattering measurements suggest that the scattering objects would have a wide variance in size distribution (8). More precise data in the range between the USANS and conventional SANS data would be needed before pursuing quantitative model fitting.

Conclusions

Neutron scattering studies of hydrides in “Dirty” and “Clean” uranium prepared with variation in hydrogen content and heat treatment show that scattering is sensitive to hydrogen content. The UH_3 -uranium scattering contrast is extremely strong and thus dominates the scattering from other phases in the uranium alloys. The characteristic size of hydrides is in the range of micrometers and appears to have a broad size distribution. The formation of hydrides is very apparently affected by the impurities in the two uranium alloys with the characteristic size being smaller in the less pure metal. An attempt to determine the amount of hydride in the purer metal from the scattering invariant gives volume fractions somewhat lower than that anticipated from chemical analysis of hydrogen. This determination depends on the assumed scattering density and was furthermore dependent on measurements in a scattering vector range where the precision was relatively low.

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REFERENCES

1. H. Inouye and A. C. Schaffhauser, “Low Temperature Ductility and Hydrogen Embrittlement of Uranium,” Oak Ridge National Laboratory, USAEC Report ONRL-TM-2563, Oak Ridge, Tennessee, July, 1969(1969)

2. V. F. Sears, Neutron Scattering Length and Cross Sections, *Neutron News*, **3** (3), 26-37 (1992)
3. A. Guinier and G. Fournet, *Small Angle Scattering of X-rays*, translated by C. B. Walker (J. Wiley, New York, NY, 1955)
4. G. Kostorz, in *Neutron Scattering*, ed. G. Kostorz, **15**, of *Treatise on Material Science and Technology*, H. Herman, series editor (Academic Press, New York, NY, 1983)
5. G.L. Powell and J.B. Condon, "Mass Spectrographic Determination of Hydrogen Thermally Evolved from Uranium and Uranium Alloys"; *Analytical Chemistry* **45**, pp. 2349-54 (1973)
6. J. R. Kirkpatrick and J. S. Bullock, IV, in press
7. J. A. Lake, *Acta Cryst.* **23**, 191-194 (1967)
8. J. J. Stephens and S. Spooner, Determination of Dispersoid Size Distribution in Inconel MA 754 by Small-Angle X-ray Scattering, *Acta Met.* **34** (2), 303-312 (1986)

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