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A row of four Shimadzu spectrophotometers is shown. From left to right: a small, compact benchtop model; a slightly larger benchtop model with a sample holder; a large, boxy benchtop model with a front-loading sample compartment; and a tall, vertical benchtop model with a large sample compartment.

# Cold neutron incoherent scattering for hydrogen detection in industrial materials

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Neutron incoherent scattering (NIS) is proposed as a method for the rapid detection of hydrogen and corrosion in industrial materials. As an example, we apply the NIS method to the detection of hydrogen in graphite and in titanium alloy, and compare the results with those obtained with the prompt gamma activation analysis (PGAA) method. The scattering cross section for hydrogen is much greater than the capture cross section, which enables the NIS method to have a detection limit and accuracy close to that for PGAA, and allows real time experiments on hydrogen detection to be performed. We report preliminary results on using the NIS method to determine hydrogen in urea [ $\text{CO}(\text{NH}_2)_2$ ]/graphite and in titanium matrices. © 1998 American Institute of Physics. [S0021-8979(98)04207-8]

## I. INTRODUCTION

A highly abundant element in the environment, hydrogen can penetrate into various materials, and even in small amounts can influence their mechanical, electrical and chemical properties. For example, at concentrations of a few tens of  $\mu\text{g/g}$  hydrogen causes embrittlement and decreased cracking strengths in steels and titanium alloys, deterioration of electrical properties in semiconductors, etc.<sup>1-4</sup> In addition, hydrogen in hydrated oxides may be one of the indicators of corrosion in metals.

Neutron methods are widely used for the nondestructive detection of hydrogen in industrial materials. These methods are based on measurements involving the various mechanisms of the neutron-proton interaction.

(1) Neutron absorption followed by the measurement of the  $\gamma$ -ray yield is used in the prompt gamma activation analysis (PGAA) method. In this technique the measurement of the intensity of the 2.2 MeV  $\gamma$  ray is performed together with a comparison with the intensities of those emitted by standard samples. For example, in the case of titanium the hydrogen detection limit can be as small as 15 to 30  $\mu\text{g/g}$ .<sup>5,6</sup> Detection at these levels (or mass fractions) requires long data collection times (a few hours) on account of the low cross section for the  $(n, \gamma)$  reaction and the large  $\gamma$ -ray background.

(2) Hydrogen and corrosion products result in a variation in the neutron refractive index, which is proportional to the coherent scattering amplitude and the atomic density. This variation is observed in experiments on neutron reflectometry, in radiography with high angular resolution,<sup>7</sup> and in small-angle scattering.<sup>8</sup>

(3) Both absorption and scattering of neutrons from hydrogen give rise to additional attenuation of the beam within the object. This is the subject of neutron radiography and tomography. Local hydrogen mass fractions higher than 1000  $\mu\text{g/g}$  can be detected by these methods in Ti alloys.<sup>9</sup>

(4) In addition, neutron scattering techniques give further possibilities for hydrogen detection. For example, the hydrogen atom fraction of only a few percent can be determined in coherent scattering experiments from the measurements of the diffraction peak intensities in crystalline materials.<sup>10</sup> However, the sensitivity of the method is poor when the crystal structure is not accurately defined.

It is well known that the incoherent scattering of neutrons from hydrogen is far stronger than both coherent scattering and absorption. Moreover, the cross section for incoherent scattering from hydrogen can be a few orders of magnitude larger than that for other elements in the matrix. For example, in Table I we present the neutron incoherent, coherent and absorption cross sections<sup>11</sup> for selected elements of industrial and technological importance, where hydrogen doping can be critical for their properties.

For hydrogen in the solid, the incoherent scattering is generally independent of the hydrogen chemical state and the crystal structure of material; it is isotropic, and can be measured away from the direct beam resulting in a low background. In addition, the use of cold neutrons allows the separation of the incoherent scattering signals from the possible diffraction peaks at thermal energies. Therefore, we can expect that incoherent scattering of cold neutrons is a convenient tool for the rapid detection of hydrogen in either trace or large concentrations. This technique has been exploited before for hydrogen determination in oil samples.<sup>12</sup> The aim of the present work is to study the possibilities of using neutron incoherent scattering (NIS) for the quantitative detection of hydrogen in industrial materials. The NIS technique depends on the difference in the scattered intensity

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TABLE I. Neutron incoherent scattering  $\sigma_i$ , coherent scattering  $\sigma_c$  and absorption  $\sigma_a$  (for  $\lambda=0.18$  nm) cross sections (in barns) (see Ref. 11), and the estimated detection limit of the hydrogen mass fraction  $c^{\Delta I=2\%}$  in  $\mu\text{g/g}$  for a 2% increase in the incoherent scattered intensity for various elements. (The value in brackets is the standard uncertainty in the last digit.)

Element	$\sigma_i$	$\sigma_c$	$\sigma_a$	$c^{\Delta I=2\%} (\mu\text{g/g})$
H	80.26(6)	1.7568(10)	0.3326(7)	...
C	0.001(4)	5.550(2)	0.00350(7)	0.02(8)
Al	0.0082(6)	1.495(4)	0.231(3)	0.08(1)
Si	0.004(8)	2.1633(10)	0.171(3)	0.035(71)
Ti	2.87(3)	1.485(2)	6.09(13)	15(1)
Fe	0.40(11)	11.22(5)	2.56(3)	1.8(5)
Zr	0.020(15)	6.44(5)	0.185(3)	0.055(41)

from an object containing hydrogen and from a similar object with no hydrogen.

## II. THEORY

Consider hydrogen of mass  $m$  homogeneously distributed within an object of mass  $M$  consisting of atoms with atomic weight  $\mu$ . Assume that the object is placed in a neutron beam with the current density  $j$  and measure the incoherent scattering intensity  $I$  with a neutron counter of area  $S$  at a distance  $R$  from the sample. If we disregard both absorption and multiple scattering, we can write

$$I = jN_A [m\sigma_i^H + (M/\mu)\sigma_i^{\text{mat}}]S/(4\pi R^2), \quad (1)$$

where  $\sigma_i^H$  and  $\sigma_i^{\text{mat}}$  are the incoherent scattering cross sections of hydrogen and the other atoms within the matrix, respectively, and  $N_A$  is Avogadro's constant. Note that the atomic weight of the hydrogen atom is carried implicitly in Eq. (1). We now evaluate the luminosity and detection limit of the method.

Let us take as the typical experimental values  $j=4 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$ ,  $S=0.5 \text{ cm}^2$ ,  $R=0.1 \text{ m}$ , and consider, for example, a titanium object of the mass 1 g with a hydrogen mass fraction  $c=m/M=500 \mu\text{g/g}$ . We obtain an intensity as large as  $10^3 \text{ s}^{-1}$ , so a counting statistical standard uncertainty less than or equal to 1% should be reached within a few seconds exposure time.

Let us calculate the hydrogen mass fraction  $c^{\Delta I=2\%}$  (where  $c=m/M$ ) that results in a 2% increase in the scattered intensity, and consider this value as a detection limit for the method. A similar conservative criterion of signal being 2% above the background has also been used for the evaluation of the detection limit in other methods.<sup>3</sup> We obtain:

$$c^{\Delta I=2\%} = 0.02(\sigma_i^{\text{mat}}/\sigma_i^H)/\mu. \quad (2)$$

The calculated values of  $c^{\Delta I=2\%}$  for different materials are presented in the Table I. In the case of titanium, for example, the detection limit of the neutron incoherent scattering (NIS) method is close to that for the PGAA method, whereas the exposure time should be much less because  $\sigma_i \gg \sigma_a$ , where  $\sigma_a$  is the cross section for hydrogen absorption, and the efficiency for neutron detection is greater than for gammas. Since the sensitivity of the NIS method depends on the value of the neutron incoherent scattering of the atoms

within the object itself, it is interesting to carry out experiments with samples having either weak or strong values of  $\sigma_i^{\text{mat}}$ .

To test the former, we have used 1 mm thick and 10 mm diameter discs from pressed graphite powder. The hydrogen mass fraction in the samples was varied from zero up to a mass fraction of 4.4% (44 mg H/g sample) by the addition of urea [ $\text{CO}(\text{NH}_2)_2$ ], with an expanded uncertainty of 0.01%, into the graphite powder. These samples are used at NIST as hydrogen standards for PGAA measurements.<sup>13</sup>

To test the latter, we have used a titanium alloy (mass fraction of 90% Ti, 4% V, 6% Al) jet engine compressor blade. Similar blades have been studied before by the PGAA method,<sup>5,6</sup> and hydrogen mass fractions have been detected in the range of 40–80  $\mu\text{g/g}$  for the new blades and 100–750  $\mu\text{g/g}$  for blades that have been previously used in an engine. In our experiments we have used the central part of a new blade where the thickness is 3.5 mm. We have simulated the extra hydrogen with effective mass fractions up to 1 mg/g by attaching to the blade surface a stack of 6  $\mu\text{m}$  thick polypropylene ( $\text{C}_3\text{H}_6$ ) films. The stack was attached to the front surface (facing the incident beam) of the blade.

## III. RESULTS

Experiments have been performed on the neutron optics facility on the NG-0 beam line<sup>14</sup> at the Cold Neutron Research Facility of the NIST nuclear reactor. A white beam of cold neutrons with an average wavelength of 0.6 nm and an aperture 5 mm in diameter were used. For the suppression of the thermal neutron fraction ( $\lambda < 0.4$  nm) of the incident beam, a 63 mm long room temperature Be filter was used in the incident beam before the sample. The scattered intensity was measured in transmission geometry with a 40 atm  $^3\text{He}$  proportional counter with an aperture of area 0.55  $\text{cm}^2$  placed 95 mm from the sample at a scattering angle of 60° (Fig. 1).

We observe that the scattered intensity increases proportionally with the hydrogen mass fraction. The high intensity is observed (500–1000  $\text{s}^{-1}$ ) as predicted earlier. At mass fractions less than 1000  $\mu\text{g/g}$  the increase is highly linear for both kinds of samples (Figs. 2 and 3), in accordance with Eq. (1). For titanium alloys the experimental value of  $c^{\Delta I=2\%}$  (16  $\mu\text{g/g}$ ) is close to the theoretical value, whereas for graphite the value (20  $\mu\text{g/g}$ ) is much higher than expected. At high ( $>1000 \mu\text{g/g}$ ) hydrogen mass fractions, however, a saturation effect starts to appear in the experimental curve (Fig. 2). We have found that experimental points for the graphite discs can be fitted well ( $R>99\%$ ) with the formula:

$$I(c) = A[1 - \exp(-c/c_0)] + I_0, \quad (3)$$

where  $A$ ,  $c_0$ , and  $I_0$  are the fitting parameters. The value of  $c_0$  for these measurements is  $(34.6 \pm 0.9) \text{ mg/g}$ , where the standard uncertainty is given. The fitting curve has been used to determine the hydrogen content of other graphite-urea disks. We have measured the intensity from these discs, and after substitution into Eq. (3), have calculated their mass fractions. To establish the accuracy of the NIS method we have compared these measured values with those measured

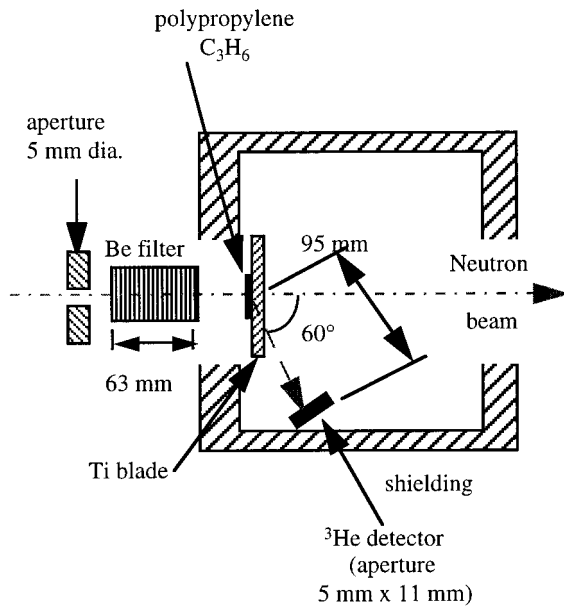


FIG. 1. A schematic diagram showing the experimental arrangement for measuring the incoherent scattering from hydrogen in samples.

by PGAA. The discrepancy is 3.5%, 0.3%, and 1.2% for the hydrogen mass fractions of 69.4  $\mu\text{g/g}$ , 13  $\text{mg/g}$ , and 44.4  $\text{mg/g}$ , respectively.

For the case of the titanium blade, we have fitted the experimental points with the linear function ( $R > 99.8\%$ ):

$$I_{\text{tot}} = I(c^{\text{extra}}) + I_b = A c^{\text{extra}} + B + I_b, \quad (4)$$

where  $A$  and  $B$  are the fitting parameters,  $c^{\text{extra}}$  is the effective mass fraction of the extra hydrogen simulated by the polypropylene films, and  $I_b$  is experimental background measured without the blade and film stack.

Let us suppose initially that the internal hydrogen of mass fraction  $c_1^{\text{int}}$  is located near the blade surface close to

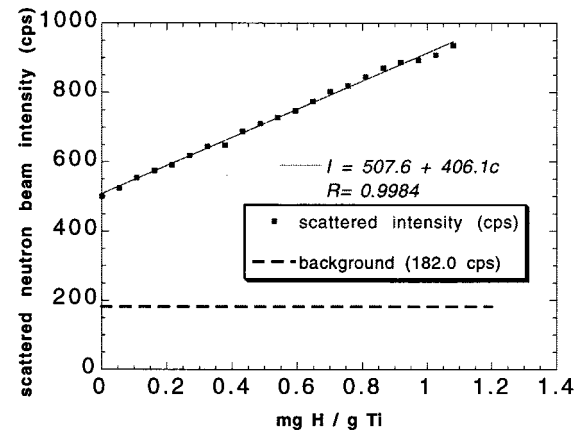


FIG. 3. Scattered intensity as a function of hydrogen mass fraction for the titanium alloys plus polypropylene films.

the film stack, otherwise we need to take neutron absorption into account. According to Eq. (1) we can write for this case:

$$I(c^{\text{extra}}) = K \{ c^{\text{extra}} + c_1^{\text{int}} + \sum_X [\sigma_i^X / (\mu_X \sigma_i^H)] \}, \quad (5)$$

where  $K$  is an unknown constant. In Eq. (5) we sum over all elements  $X$  within the blade. From Eqs. (4) and (5) we obtain

$$c_1^{\text{int}} = B/A - \sum_X [\sigma_i^X / (\mu_X \sigma_i^H)]. \quad (6)$$

Using the measured value for  $B/A = (802 \pm 16) \mu\text{g/g}$  and the calculated value for  $\sum_X [\sigma_i^X / (\mu_X \sigma_i^H)] = (722 \pm 7) \mu\text{g/g}$ , we find a hydrogen mass fraction  $c_1^{\text{int}} = (80 \pm 18) \mu\text{g/g}$ , where the  $\pm$  values are the standard uncertainties.

Now, let us suppose that the internal hydrogen is located at the back surface (opposite to the stack) and take into account the neutron absorption within the Ti alloy itself. In the case of a planar sample we can find a new value:

$$c_2^{\text{int}} = c_1^{\text{int}} \exp[\mu_{\text{abs}} t (1 - \sec \alpha)], \quad (7)$$

where  $t$  is the thickness of the blade,  $\mu_{\text{abs}}$  the linear absorption coefficient, and  $\alpha$  is the scattering angle. If we substitute  $\mu_{\text{abs}} t = 0.40$ ,  $\alpha = 60^\circ$ , we obtain  $c_2^{\text{int}} = (54 \pm 15) \mu\text{g/g}$ . In practice we do not know the real location of the hydrogen within the blade. Therefore, the hydrogen mass fraction  $c^{\text{int}}$  in the blade can be estimated as the average of  $c_2^{\text{int}}$  and  $c_1^{\text{int}}$ , the mass fractions in the two extreme cases,  $c^{\text{int}} = (67 \pm 15) \mu\text{g/g}$ . This value is within the range of mass fractions measured in new blades by the PGAA method,  $(54 \pm 18) \mu\text{g/g}$  to  $(61 \pm 18) \mu\text{g/g}$ .<sup>6</sup> Note that the uncertainty is partially attributed to the method for correcting for absorption within the Ti blade. The path length of the scattered neutrons can be reduced by using small scattering angles, and thereby reducing the influence of absorption on the accuracy of the measurements.

We now discuss the reason for the discrepancy in the experimental and calculated values of  $c^{\Delta I=2\%}$  for the graphite discs. We find that the explanation is the neutron scattering in the graphite itself. Scattering was observed above the background in the sample for zero hydrogen concentration and is unlikely to be associated with incoherent scattering because  $\sigma_i$  for graphite is practically zero. The reason for this effect is probably inelastic neutron scattering. In graphite

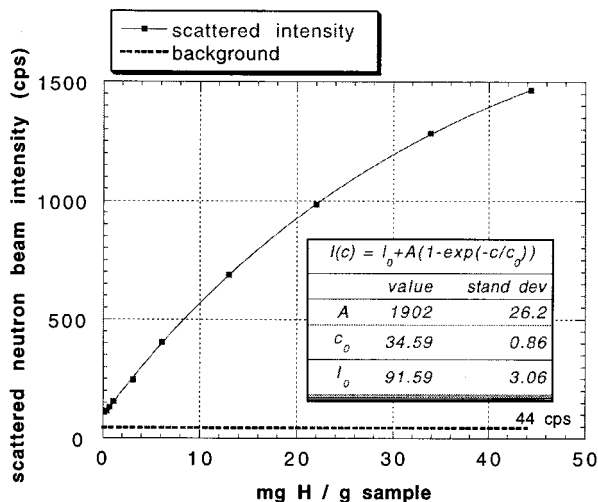


FIG. 2. Scattered intensity as a function of hydrogen mass fraction for the urea-graphite powder samples.

the coherent inelastic scattering should be much stronger than in Ti because of the small atomic mass of carbon and its large coherent scattering amplitude. Consequently, cooling the sample can reduce this scattering.<sup>15</sup>

#### IV. CONCLUSIONS

We conclude that the neutron incoherent scattering method can be usefully applied for the real time determination of hydrogen mass fractions in various matrices of both low and high incoherent scattering cross sections. The method is both simple and practical. The first experiments on graphite and titanium demonstrate that the method has a detection limit of 15–20  $\mu\text{g/g}$ , close to that for the PGAA method, and is much better than other neutron techniques (radiography, coherent scattering, etc). In addition, the exposure time for NIS is much less. However, the incoherently scattered intensity itself contains no information about the specific type of atom from which it originates. This atom-specific information is derived only by comparing the scattered intensity with the theoretical value for different atomic compositions. This works well for the titanium blade measurements because the scattering from the object with no hydrogen can be calculated accurately, by simply using the incoherent cross sections and the known composition of the blade. On the other hand, this approach does not provide the expected sensitivity when applied to the graphite sample. This discrepancy is attributed to the coherent scattering from the graphite. Such coherent scattering effects may be significant for some other industrial materials if filtering of the thermal fraction of the beam is not complete. This requires a more careful treatment in greater detail before the incoherent scattering technique can be routinely used for quantitative analysis. In addition, the lack of reliable knowledge of the composition of real industrial materials may limit the accuracy with which the amount of hydrogen can be determined.

Despite these difficulties, the NIS method has important potential applications to industrial research problems. In particular, it can be applied in combination with other methods of hydrogen detection for the investigation of hydrogen and radiation embrittlement and hidden corrosion in industrial

materials (Fe, Ti, Zr, Al). In combination with neutron focusing systems, for example, with capillary lenses,<sup>16,17</sup> the NIS method can allow a scanning of the sample to determine the local hydrogen mass fraction as a function of position. Future measurements may include the determination of the depth distribution and mass fraction of hydrogen within titanium blades.

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