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13. ABSTRACT (Maximum 200 words) The objective of the proposed research is to conduct several preliminary experiments to verify calculations made by these investigators that show it to be possible to non-destructively and quantitatively determine hydrogen content in steel and possibly other host materials at the parts per million level (minimum level of from 100 to 1 ppm). The hydrogen analysis is based on the fact that 24 keV neutrons readily penetrate large thicknesses of materials composed mainly of iron with little scattering and the scattering that does occur, is nearly isotropic. (Cont'd on reverse side)					
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However, the presence of a light material (small mass number) such as hydrogen will cause significant scattering of the neutrons in a preferred forward angle, which permits these hydrogen-scattered neutrons to be distinguished from other neutrons by their particular scattering angle and energy. The number of neutrons scattered at angles and energies peculiar to hydrogen will be directly proportional to the concentration of hydrogen in the host material. Thus, the measurement of the number of hydrogen-scattered neutrons will permit the quantitative, non-destructive measurement of the hydrogen concentration in test articles or samples and/or whole prototypes; these materials can subsequently be subjected to physical measurements to determine the effect of various levels of hydrogen concentrations on the engineering properties of the host material.

Non-Destructive Analysis for Hydrogen Concentrations in Materials

Final Report

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1. STATEMENT OF PROBLEM STUDIED

The objective of the proposed research was to conduct several preliminary experiments to verify calculations made by the principal investigators to show the possibility of non-destructively and quantitatively determining hydrogen content in steel and possibly other host materials at the parts per million level (minimum level of from 100 to 1 weight ppm). The hydrogen analysis was based on the fact that 24 keV neutrons readily penetrate large thicknesses of materials composed mainly of iron with little scattering and the scattering that does occur is nearly isotropic. However, the presence of a light material (small mass number) such as hydrogen causes significant scattering of the neutrons in a preferred forward angle, which permits these hydrogen-scattered neutrons to be distinguished from other neutrons by their particular scattering angle and energy. The number of neutrons scattered at angles and energies peculiar to hydrogen is directly proportional to the concentration of hydrogen in the host material.

2. SUMMARY OF IMPORTANT ISSUES

The objective of the research was to detect hydrogen at a concentration of 1 weight per million (a concentration of approximately 4.74×10^{18} atoms of H per/cm³) in bulk samples of high strength steel. This range of concentration was determined through discussions with personnel from:

- * U.S. Army Materials Technology Laboratory, Watertown, MA
- * State University of New York at Albany
- * Naval Air Development Center, Warminster, PA

Uncertainties in the range of 1 weight ppm down to 0.2 weight ppm (55.4 to 11.1 atoms ppm) were achieved as a result of our experiments. A further objective was to develop a technique that would be applicable to bulk samples displaying the engineering properties of the host material.

Based on an extensive and intensive search of the recent neutron spectroscopy literature as well as the experience of the researchers, the spherical hydrogen filled proton recoil neutron (Benjamin) spectrometer was selected as best suited, of available spectrometers, to the requirements of this work. The Benjamin is well suited to the neutron energy region of interest (less than 1 to 24 keV) and is capable of discrimination between neutron and gamma ray induced events.

Initial experimental measurements showed that gamma rays present in the reactor generated neutron beam were scattering off the sample and other objects in the vicinity of the Benjamin spectrometer. These scattered gamma rays were detected by the spectrometer and although the detector could discriminate between gamma rays and neutrons, when the gamma ray intensity relative to the neutron intensity is sufficiently high, there was interference with

analysis of the neutron spectrum. A gamma ray shield was designed and fabricated. Experiments showed that the gamma ray background was reduced by a factor of about 10. Although additional shielding could further reduce gamma ray intensity, it did not appear necessary.

Further experiments showed that increasing the hydrogen pressure in the Benjamin spectrometer would improve the neutron detection efficiency relative to gamma rays. Increasing the hydrogen pressure to four atmospheres should theoretically increase the hydrogen detection efficiency by about a factor of four.

Experiments also indicated a proton interference problem within the Benjamin spectrometer detector after it was exposed to radiation for a period of time. Further, results indicated a lower limit of detection (LLD) of 300 atom ppm (5.4 weight ppm). Although some experimental parameters could be changed to lower this lower limit, improvements would be unlikely to allow 1 (atom) ppm measurements.

Notched spectrum and iron filter techniques were evaluated as an alternative to the Benjamin detector. The notched spectrum approach developed at KAPL in 1969 exhibited a high sensitivity for hydrogen in plastic samples using activation foils to detect the thermal neutrons. There was sufficient experimental data to indicate a LLD of 150 atom ppm (0.90 weight ppm) using the current, preliminary experimental setup for the notched spectrum technique. In addition to the lower LLD, there was potential to decrease this limit, whereas improvements in the Benjamin spectrometer measurements were limited. Preliminary theoretical calculations indicated that the signal to noise ratio for the notched filter technique could be in one order of magnitude larger than that given above which would lower the LLD to approximately 50 (atom) ppm. The sensitivity of the technique was primarily limited by the ability to shield the activation foils used to measure the hydrogen and iron concentrations) from background neutrons in the experimental area. This technique is being examined at INEL to determine the amount of hydrogen (in the ppm range) in zirconium.

Important parameters considered included the "purity" of the neutron spectrum in the neutron beam, and the level of activation of the foils which determines the uncertainty in the measurement. Following preliminary calculations, an Indium filtered beam was fabricated and installed at the University of Missouri Research Reactor.

Initial measurements indicated a signal-to-noise ratio (i.e. hydrogen signal vs iron signal) comparable to that obtained using the Benjamin spectrometer system. For example, experimentally measured hydrogen/iron signal ratios were on the order of 0.007 for a sample containing 100 (atom) ppm of hydrogen using the Benjamin spectrometer system. Additionally, the process of extracting the signal from the noise (unfolding the neutron spectrum) is inherently prone to additional statistical variations. Similar measurements in initial experiments (which were relatively crude) using the notched filter indicated essentially the same ratio (0.005) for the same sample and no unfolding process was required.

In support of theoretical calculations of the sensitivity of the notched filter techniques, preliminary experiments were completed using a neutron beam filter tube containing a 10 cm thickness of indium in a beam tube of the MURR. Thin foils were fabricated by alloying indium and lead, which were subsequently counted on a 7.5-cm BGO detector. A sample, consisting of a relatively thick (0.8-cm thick sample of iron and a thin (0.008-cm thick) plastic sheet, was used for these measurements. The effect of not placing the activation foils in the neutron beam resulted in a threefold reduction in the activity of the background foil. These experimental data indicated, however, that sensitivities of 100 atom ppm (1.80 weight ppm) of hydrogen in thick samples of iron were possible and sensitivities below 10 atom ppm (approximately 0.2 weight ppm) should be possible with optimization of beam purity, beam strength, background neutron shielding, activation foil thickness, and counting geometry. These predicted levels of detection were achievable because of the high neutron flux available at the MURR and because of the beam facilities that can accommodate this modified notched filter method.

Additional work resulted in a more accurate quantification of the sensitivities of the two methods for experimentally measuring hydrogen in steels or other metals. The sensitivity of the iron filtered beam technique was reduced to approximately 500 atom ppm (9 weight ppm in steel) and the notched filtered beam technique was sensitive to approximately 600 atom ppm (11 weight ppm).

To further increase this sensitivity, new experimental methods were designed for both methods. The iron filtered beam technique was improved by the addition of a "large area" detector system made up of six, cylindrical detectors. This system was designed to detect all neutrons scattered in the azimuthal angle. This will increase the detection efficiency by a factor of 35, thereby increasing the sensitivity to hydrogen by approximately a factor of 6 down to less than 100 atom ppm (approximately 2 weight ppm). The new system was implemented in the Spring, 1991.

For the notched filter technique, a new beam was designed that would increase the neutron flux by a factor of 15. The detection foils were modified to increase the sensitivity to hydrogen. Theoretical calculations showed that the sensitivity could be increased to the 10 atom ppm (0.2 weight ppm) level, but this needed to be confirmed with new experimental measurements.

Work also progressed towards development of a pulse system for proton recoil neutron spectroscopy applicable to the neutron scattering technique for measuring total hydrogen. An indepth review of the literature to evaluate various techniques for measuring mobile and total hydrogen and the relation between these hydrogen concentrations and the engineering properties of the metals was completed.

The review of the literature (over 1,000 citations) was prompted by the knowledge that the mechanical properties of different steels could be adversely affected by different

concentrations of hydrogen. High strength steels will become brittle to the point of ready fracture for hydrogen at concentrations greater than 1 weight ppm (55.4×10^{18} atom ppm). Stainless steel and mild steels will tolerate much higher concentrations (about 200 ppm) of hydrogen before they will experience brittle fracture. However, documentation on the quantitative affects of hydrogen on particular steels was not readily available. There was difficulty in interpreting information from the literature in terms of the impact of hydrogen concentration on the engineering properties of the metal. There was a general consensus that it is mobile hydrogen that produces the brittle fracture of steel with which we are concerned. However, there is little information relating mobile hydrogen concentration to degradation in engineering properties. We collected available information and rationalized methods of measuring mobile hydrogen concentration, total hydrogen concentration and the units used by various authors to express the concentration.

In Summer 1991, a modified, notched neutron spectrum technique was tested with calculations and experimental measurements. The results indicated that hydrogen content in steel could be measured with an experimental precision greater than 20 atom ppm or 0.4 weight ppm. Calculations indicated that this ultimate sensitivity is a function of the thickness of the sample, the thickness of the filter, and the geometry of the foils. The experiemtns indicate that the positioning of the sample between two foils is crucial in determining the absolute uncertainty in experimental measurements.

The precision of the 0.4 weight ppm is representative of a "typical" sample and may be somewhat more or less for other samples. Optimization of various parameters (i.e. filter thickness, effective foil thickness, may be necessary to achieve the best sensitivity for a given sample material or thickness.

This technique has utility for a wide variety of applications in which the amount of hydrogen content in a material (or a hydrogen containing coating on a material) is critical. The measurement process is straight-forward, nondestructive, and provides a new analytical tool

for determining hydrogen content.

ACKNOWLEDGEMENTS

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3. LIST OF PUBLICATIONS AND TECHNICAL REPORTS

Publications

Miller, W.H. and W. Meyer, "Experimental Neutron Spectroscopy Down to 1 keV," Tran. Am. Nucl. Soc., Vol. 59, pp. 132-134 (June 1989)

Meyer, W. and W.H. Miller, "Nondestructive Analysis for Hydrogen In Steel Using Neutron Scattering," Trans. Am. Nucl. Soc., Vol. 59, pp. 137-138 (June 1989). *Awarded the Significant Contribution Award by the American Nuclear Society Material Science and Technology Division..*

Miller, W.H., "Neutron Spectroscopy In The 1 to 30 keV Energy Range," Nuclear Instruments and Methods in Physics Research, A-279, pp. 546 - 544 (1989).

Miller, W.H., R. Brugger and W. Meyer, "Modified Notched Filter Technique For Determining Hydrogen in Metals," Trans. Am. Nucl. Soc., 61, pp. 102-103 (June 1990).

Miller, W.H. and K. McCollough, "An Integrated, Pulse Shape Analysis System for Proton Recoil Neutron Spectroscopy," Seventh Symposium on Radiation Measurements and Applications, University of Michigan (May 21-24, 1990). Also to be published in Nuclear Instruments and Methods.

Miller, W.H., A. Kumar and W. Meyer, "New Techniques for Measuring Low Levels of Hydrogen or Hydrogen Bearing Materials in Solids," Submitted for review to Journal of Nondestructive Evaluation (June 1991).

Miller, W.H., L-T Lin, R.M. Brugger, W. Meyer, "Detection of PPM Levels of Hydrogen in Solids

Using a Modified Notched Neutron Spectrum Technique," submitted to Nuclear Technology (September 1991) and Nuclear Instruments and Methods (September 1991).

Workshops

Meyer, W. and W. H. Miller, "Neutron Energy Loss Spectroscopy for Nondestructive Analysis of Hydrogen Materials," Workshop on Surface Science and Technology, University of Michigan - Ann Arbor, Michigan (Nov. 7, 1990).

Proposal

Draft proposal, "A DSP-Based, Smart Analog-to-Digital Converter for Nuclear Radiation Detectors," submitted November 1990.

Report

A. Kumar, "Measurement of Hydrogen in Steels Using Modulated Beam Mass Spectrometry," February 1990.

4. PARTICIPATING SCIENTIFIC PERSONNEL

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MS Nuclear Engineering, December 1990

MS thesis title - "Neutron Spectra Estimation Using a Cylindrical Proton Recoil Detector."

Alan Bako

MS Nuclear Engineering degree in progress

Tean-Jean (Vincent) Chuang

MS Nuclear Engineering, March 1991

MS thesis title, "The Neutron Notched Spectrum for Determining Densities of Hydrogen in Steel"

Li-Te (Steven) Lin

MS Nuclear Engineering, May 1991

MS thesis title - "Monte Carlo Analysis of the Notched Filter Technique for the Measurement of Low Hydrogen Content in Iron."

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MS Nuclear Engineering degree in progress

tentative MS thesis title, "A Comparison of MCNP Monte Carlo Calculations and Experimental Measurements for the Notched Filter Technique."