MODULATED-BEAM MASS SPECTOMETRY SYSTEM FOR THE DETERMINATION OF LOW LEVELS OF HYDROGEN IN IRRADIATED MATERIALS - B. M. Oliver, J. A. Abrefah, F. A. Garner (Pacific Northwest National Laboratory)*, and A. Kumar (University of Missouri, Rolla)

OBJECTIVE

To develop a hydrogen analysis system for the determination of low levels of hydrogen in irradiated materials.

SUMMARY

A high-sensitivity analysis system has been developed for the measurement of hydrogen in solid materials. The system is based on a low-volume hot crucible hydrogen extraction furnace in combination with a modulated-beam quadrupole mass spectrometer detector system. Calibration of the system is conducted using a commercially available hydrogen leak source attached to the detector volume input line. Initial tests on the system using 5 to 10 mg sized specimens cut from a hydrogen-containing steel standard of 5.2 ± 0.3 wppm gave an average concentration of 5.8 ± 0.2 wppm. The ultimate system detection limit is currently ~5 x 10^{14} atoms, or ~5 appm for a 10 mg specimen. Future work will now involve analysis of a number of irradiated materials from various fission and fusion research programs.

PROGRESS AND STATUS

Introduction

Starting in 1997, tests were carried out at Pacific Northwest National Laboratory (PNNL) for the purpose of fabricating a furnace/analysis system to measure hydrogen gas generation in 1) target and cladding materials proposed for the Accelerator Production of Tritium (APT) program, and 2) various materials of interest to the U.S. Fusion Materials Program and the U.S.-Japan JUPITER program. An initial system was developed which permitted the measurement of hydrogen in tungsten material irradiated in an 800-MeV proton beam[1]. This initial system was based on isotope-dilution static-mode gas mass spectrometry, which is the basis for an existing system at PNNL for the measurement of very low levels of helium in irradiated materials[2]. Although this system provided useful initial data to the APT program, the system could only be used for relatively high hydrogen levels (thousands of appm), and the absolute accuracy of the system was difficult to assess.

In order to improve on the accuracy and sensitivity of hydrogen measurements at PNNL, a second development effort was undertaken which involved improvements to both the sample hydrogen extraction and detector components. The hydrogen extraction system improvements involved significantly reducing the volume and type of materials in the sample furnace that were heated and in direct connection to the mass spectrometer detector. The detector improvements involved a redesign of the detector based on a technique known as modulated-beam mass spectrometry (MBMS)[3]. The MBMS technique involves chopping the

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input gas flow to the mass spectrometer using a chopper blade, and then using a lock-in amplifier to detect the resulting modulated hydrogen signal from the much larger background "dc" hydrogen signal emanating from the detector volume.

Hydrogen Extraction System

A schematic diagram of the hydrogen analysis system is shown in Figure 1, with the sample extraction furnace shown on the left side, and the MBMS detector system on the right. Hydrogen is extracted from the analysis samples by heating to temperatures up to ~1200°C. The extraction furnace consists of a sample turntable assembly located above a boron nitride "test-tube" shaped crucible heated on the outside by a resistance-heated tungsten filament. Samples are loaded into the upper section of the turntable and remotely dropped through the central vertical channel into the crucible using a bellows-sealed pusher rod. The upper section can be isolated, vented, and then vacuum pumped to allow for sample loading while the crucible is maintained under vacuum heating. The top view-port section is sealed to the turntable section using a double o-ring seal with differential pumping between the o-rings. Connection to the hydrogen detector system is through a side vacuum channel located below the isolation gate valve.

The tungsten heating filament is contained inside a water-cooled copper enclosure connected to its own separate vacuum system. The upper sample/viewport section is sealed to the lower copper-block section using the same type of double o-ring seal used in the upper section. Currently, the crucible temperature range is ~750°C to ~1200°C and is determined using an optical pyrometer through the upper viewport. Temperature uncertainty is estimated to be ±50°C. A near-term improvement to the system will be the addition of direct thermocouple measurement of the temperature which will permit more accurate temperature determination, and allow for stepped-anneal or ramped hydrogen release measurement.

Hydrogen Detector System

The hydrogen detector system is shown in the right hand side of Figure 1. An isolation valve and quick-disconnect VCR-type® fitting are provided in the gas line from the extraction furnace to allow for easy access to the lower water-cooled copper chamber for crucible or heater replacement. Hydrogen gas flow from the extraction system travels through the horizontal vacuum line and is interrupted by the rotating six-blade chopper wheel, which periodically "blocks" and "unblocks" the direct movement of the hydrogen gas to the ionization region of the detector. The rotational frequency of the chopper blade is controlled by an ultra-high vacuum stepper motor and external controller. The rotational speed of the motor can be varied to provide chopping frequencies up to ~120 Hz.

The mass spectrometer detector is a standard quadrupole analyzer with both faraday cup and electron multiplier detectors. For the present application, the direct output of the electron-multiplier is fed to a lock-in amplifier which is synchronized to the chopper frequency. Synchronization is provided by a square-wave output signal from an infrared emitter-detector assembly located around the lower section of the chopper wheel. Calibration of the MBMS system is performed using an external calibrated hydrogen leak attached to the vacuum line from the extraction system. This calibrated leak has a very small trapped volume, resulting in virtually no lowering of the leak rate with time.

Initial System Tests

Initial tests have been conducted on the system to allow for optimization of the various system parameters including, chopping frequency, mass spectrometer ionizer parameters, and lock-in amplifier settings. These initial tests were conducted using small stainless steel samples cut from material[1] with a known hydrogen content of 5.2 ± 0.3 wppm (equivalent to 285 appm H) at a system crucible temperature of ~1200°C. The form of the standard material was rods, ~4 mm in diameter and ~10 mm in length. Samples for analysis were obtained from slices cut from the rods using a slow-speed Isomet® saw both with and without water cooling. From each cut slice, four or five analysis specimens were then cut using small diagonal cutters. Prior to analysis, each specimen was ultrasonically cleaned in acetone, air dried, and then weighed using a NIST traceable microbalance.

The results of the initial hydrogen analyses are given in Table 1. Column 2 in Table 1 indicates the cutting method employed for each specimen. The hydrogen release curve for Sample SS501-13 is also shown in Figure 2 as an example. Two release peaks are evident as the sample quickly heats to the crucible temperature of ~1200°C. The results of the six analyses indicate an average measured hydrogen content in the steel of 5.8 wppm, with a standard deviation in the measurements of ~3%. Compared to the stated content of the steel, the present results show an average bias of +12%, although the measured value is within the 2σ uncertainty of the standard. This possible bias is also within the stated ±15% uncertainty of the calibrated leak used to obtain the absolute sensitivity for the MBMS system. Additional analyses of different standard samples may permit an adjustment in the calibrated hydrogen leak value, resulting in improved absolute uncertainty estimates.

Hydrogen background levels in the system are currently limited by dissociation of residual water from the room-temperature parts of the system by the hot crucible. This background level drops significantly for crucible temperatures of ~1000°C, and this lower temperature may be sufficient for complete hydrogen release in steels. Addition of a water vapor cold trap to the upper sample section is also being considered. At the present hydrogen background levels, the lower sensitivity limit for the system is ~5 x 10^{14} atoms of hydrogen release. This is equivalent to ~5 appm in a 10 mg size steel sample.

FUTURE WORK

Following confirmation of system sensitivity and reproducibility, hydrogen analyses will be conducted on Inconel 718 and additional tungsten samples from the APT program, as well as a variety of samples from U.S. and U.S.-Japan JUPITER fusion materials programs, including isotopically-tailored ferritic alloys, SiC composites, vanadium alloys, and reactor steels.

REFERENCES

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MODULATED-BEAM HYDROGEN ANALYSIS SYSTEM

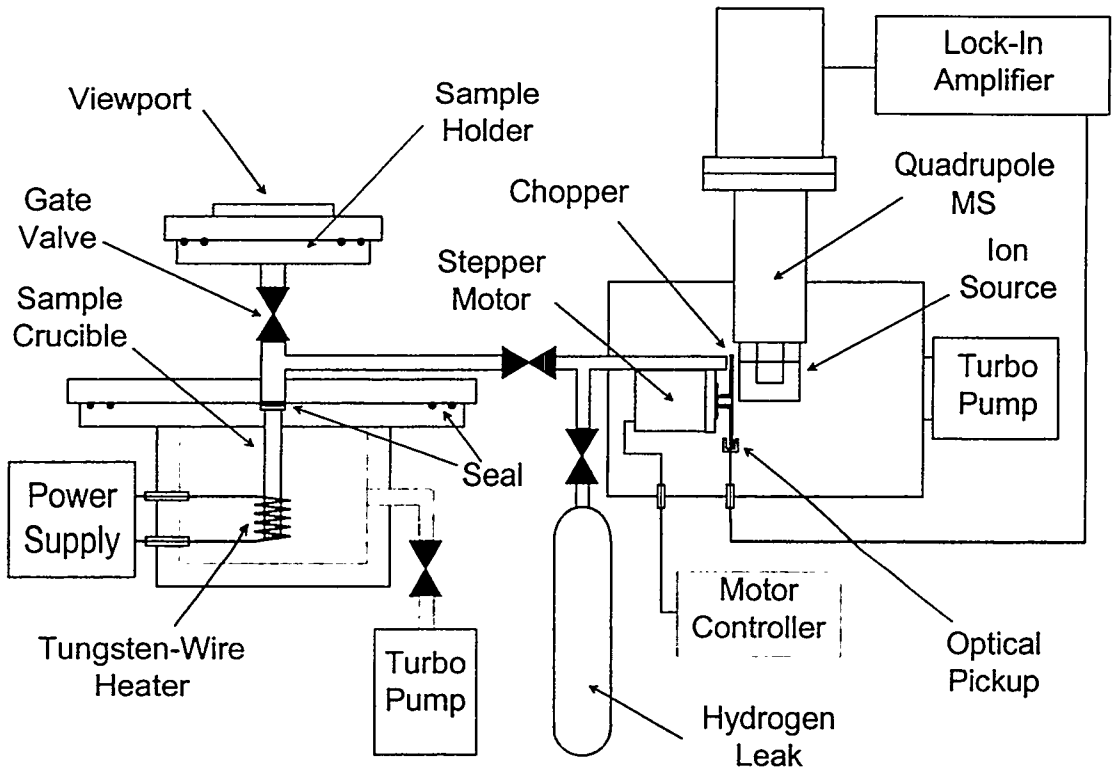

Figure 1. Schematic Diagram of Hydrogen Analysis System

Table 1. Measured Hydrogen Contents in Test Steel Samples

Sample	Cutting Method	Mass (mg)	Measured Sensitivity (V·s/mole)	Integrated Hydrogen Release (V·s)	Calculated Hydrogen Concentration (wppm)
SS501-17	dry	6.59	1.15E-02	6.24E+05	5.66
SS501-18	dry	7.02	1.22E-02	5.98E+05	5.88
SS501-11	wet	7.34	1.19E-02	5.88E+05	5.56
SS501-12	wet	7.48	1.29E-02	5.74E+05	6.07
SS501-16	dry	5.31	9.96E-03	6.48E+05	5.83
SS501-13	wet	9.37	1.74E-02	6.45E+05	5.80
				Mean	**5.8**
				1σ	**±3.1%**

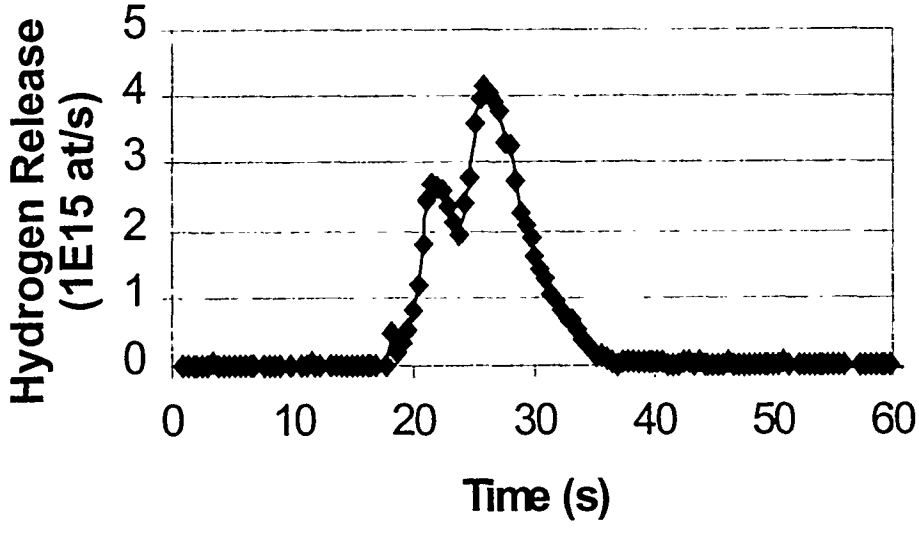

Figure 2. Hydrogen Release Curve for Sample SS501-13