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High-sensitivity quadrupole mass spectometry system for the determination of hydrogen in irradiated materials

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Abstract

High levels of helium and hydrogen are generated in metals in fusion reactors, and fusion simulations in mixed-spectrum fission reactors, spallation neutron sources, and high-energy charged particle environments. Although hydrogen generation rates are generally higher than those of helium, hydrogen is thought to quickly diffuse out of metals, especially at elevated temperatures. There appear to be some conditions, however, where significant hydrogen retention can occur. To assess this potential, a high-sensitivity analysis system has been developed for the measurement of hydrogen in small samples of irradiated materials. The system is based on a low-volume extraction furnace in combination with a quadrupole mass spectrometer, and has a detection limit of ~1 appm for steel. Hydrogen levels have been measured in high-energy proton-irradiated tungsten and Inconel 718, in iron-based alloys and vanadium alloys from fusion materials programs, and in stainless steels and pure metals irradiated in light water reactors. Details of the system and typical results are presented. © 2000 Elsevier Science B.V. All rights reserved.

1. 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 retention in target and cladding materials proposed for the accelerator production of tritium (APT) program, and in various materials of interest to the US fusion materials program and the US-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 system was based on isotope-dilution, static-mode, gas mass spectrometry, similar to 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 particular, background hydrogen levels in the detector were difficult to determine.

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 complete redesign of the detector volume to minimize its size and its proximity to the extraction furnace. Also incorporated into the detector design was a chopper blade assembly to permit measurements using a modulated-beam (MB) technique. The MB technique involves chopping the input gas flow to the mass spectrometer, and then using a lock-in amplifier to detect the resulting modulated hydrogen signal. This technique is useful for situations where the background hydrogen levels in the detector volume are comparable or larger than levels being released from the analysis samples.

2. Hydrogen extraction system

A schematic diagram of the hydrogen analysis system is shown in Fig. 1. Hydrogen is extracted from the

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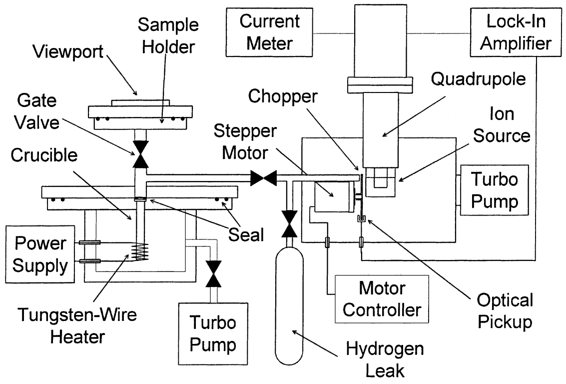

Fig. 1. Diagram of hydrogen analysis system.

analysis samples by heating to temperatures up to ~1200°C. The extraction furnace shown on the left-hand side consists of a sample turntable assembly located above a ceramic 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 push 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 glass 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 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 section is sealed to the lower copper-block section using the same type of double o-ring seal used for the viewing glass. Currently, the crucible temperature range is ~750–1200°C and is determined using an optical pyrometer sighting through the upper viewport. The temperature uncertainty is estimated to be ±25°C based on comparison of pyrometer readings with direct thermocouple measurements taken on the inside of the crucible.

3. Hydrogen detector system

The hydrogen detector system is shown in the right-hand side of Fig. 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. The detector volume is a standard six-port high-vacuum stainless steel chamber. The feed tube from the hydrogen extraction furnace enters the chamber through one of the side ports, and the quadrupole assembly is attached through the top port. The chamber is continuously pumped using a turbomolecular pump attached to the rear port of the system. System pressure is monitored using an ionization gauge connected to one of the remaining ports. A viewport is located on the front port to allow viewing of the quadrupole detector assembly and chopper system.

Hydrogen gas flow from the extraction system travels through the horizontal vacuum line which terminates very near the ionization region of the quadrupole detector. The chopper blade, for modulated beam measurements, is located between the end of the inlet tube and the detector, and periodically 'blocks' and 'unblocks' the direct movement of the hydrogen gas to the ionization region of the detector. The rotation 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 quadrupole analyzer with both faraday cup and electron multiplier detectors. For the present application, the output of the electron-multiplier is fed either to the lock-in amplifier, which is synchronized to the chopper frequency, or fed directly to a digital multimeter (DMM). Synchronization of the lock-in is provided by an infrared emitter-detector assembly located around the lower section of the chopper wheel. The DMM is interfaced to an IBM-compatible PC for data collection and analysis. The computer is also used to control the operation of the quadrupole detector. For MB operation, output from the lock-in amplifier is measured by the DMM.

4. Hydrogen measurement procedure

Hydrogen analysis specimens are prepared by cutting small replicate specimens from the material of interest. Prior to analysis, each specimen is individually cleaned in acetone and air-dried. The mass of each specimen is then determined using a microbalance with an uncertainty of ~0.002 mg.

Samples for analysis are loaded into the sample holder carousel located above the extraction furnace. Before initial vacuum pumping, the sample chamber and crucible volume are subjected to a low-pressure (~200 mTorr) argon gas discharge to aid in desorption of water or hydrated-oxide surface layers that could be dissociated by the hot crucible during analysis, and thus contribute to the measured hydrogen release. Following this procedure, the crucible and sample area are pumped down and then opened to the analysis chamber. The crucible is then pre-heated to approximately 1000°C under high vacuum for a minimum period of ~18 h. Several hours before the analyses, the crucible temperature is raised to 1200°C. During the pre-heating and subsequent analyses, the sample chamber is maintained at room temperature. Sample analyses are conducted by dropping the individual specimens into the heated crucible sequentially. Hydrogen release, in terms of current output from the electron multiplier, is measured as a function of time. Total hydrogen released is determined from the integral of the hydrogen release curve and the measured system sensitivity.

5. System calibration and uncertainty

Calibration of the system sensitivity is accomplished using a hydrogen leak source attached to the vacuum line between the extraction furnace and the detector volume. The leak rate of the source is 1.03×10^{-10} mol H_2/s (1.24×10^{14} atoms/s) with a stated uncertainty of ±15% (3σ). This calibrated leak has a very small trapped volume, resulting in virtually no lowering of the leak rate with time. Calibration measurements are conducted before and after each sample analysis, and show an overall reproducibility of ~2–3%. A typical plot for the hydrogen leak source is shown in Fig. 2. Here, the background signal for the quadrupole is ~0.5 nA. The signal increases to ~1 nA with the hydrogen leak valve open. Each of the data points represents an average of 20 measurements by the DMM. The data sampling rate is approximately two samples per second.

Absolute uncertainty (1σ) in the hydrogen analyses is currently estimated at ~20%, and is due partly to the uncertainty in the calibrated hydrogen leak source. The system has been determined to be linear up to a total hydrogen release of at least 10^{17} atoms, which for a 0.5 mg steel sample, represents a hydrogen concentration of ~20 000 appm. Additional uncertainty may also be present from possible hydrogen release from remaining water layers or hydrated metal oxides on the surface of the sample that are subsequently dissociated by the hot crucible. It is hoped that with more experience with the system, this uncertainty will be reduced.

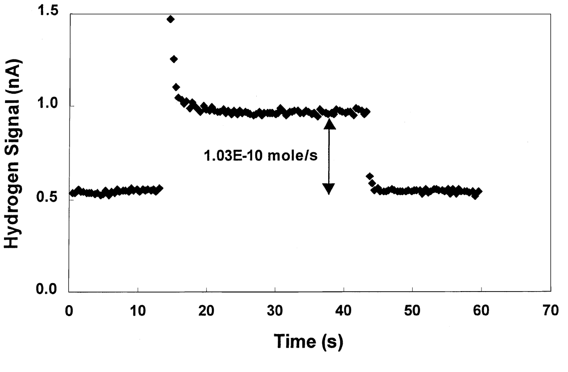

Fig. 2. Calibration signal from hydrogen leak source.

Measurements are also routinely conducted on specimens of a standard, hydrogen-containing steel maintained in the laboratory. The form of this standard material is rods, ~4 mm in diameter and ~10 mm in length. Specimens for analysis are obtained from slices dry-cut from the rods using a slow-speed saw. From each slice, 5–10 specimens are cut, resulting in sample masses ranging from ~2 to 8 mg. The stated content of the steel is 5.2 ± 0.3 wppm. The average hydrogen content measured in more than 90 of these samples is 5.4 wppm with a reproducibility of ~30% (1σ). It is speculated that the variability observed in the standard samples is associated with actual heterogeneity in the hydrogen content at this small mass level.

6. Hydrogen measurements on irradiated materials

Hydrogen measurements have been conducted on tungsten [1,3], Inconel 718 [4,5], and 300 series stainless steels [5] irradiated at a spallation source with 600–800 MeV protons mixed with lower energy neutrons. Measurements have also been made on iron-based alloys [6], vanadium alloys [7], and pure Ni and Fe from the US and US-Japan JUPITER fusion materials programs in HFIR and ATR [8]. Hydrogen levels measured in these materials have ranged from ~50 to ~16 000 appm, for sample masses from as low as 0.3 mg up to ~10 mg, depending on the estimated hydrogen levels and radioactivity levels.

A typical hydrogen release curve at 1200°C for an ~0.6 mg sample of Inconel 718 irradiated to ~1.4 dpa at 35°C with spallation neutrons and protons is shown in Fig. 3(a), plotted versus time. Each of the data points represents an average of 40 measurements, with a sampling rate of approximately six data points per second. Hydrogen release occurs over a relatively short time period of ~10 s, with a rapid initial release followed by a somewhat slower decay tail. Total integrated hydrogen release for this sample was 1.06×10^{16} atoms, or 1760 appm.

Hydrogen measurements have also been conducted using an approximately linear temperature ramp for hydrogen release kinetics studies. For these measurements, the crucible temperature was increased from ~250°C to 1200°C in a time period of ~400 s. Figs. 3((b),(c),(d)) show ramped release behavior for Inconel 718 (spallation protons, neutrons, ~1.4 dpa, 35°C), pure nickel (HFIR, 44 dpa, 400°C), and PCA (HFIR, 33 dpa, ~400°C), respectively. Total atoms of hydrogen released and calculated hydrogen concentration are listed in each plot. Note that while the 718 and

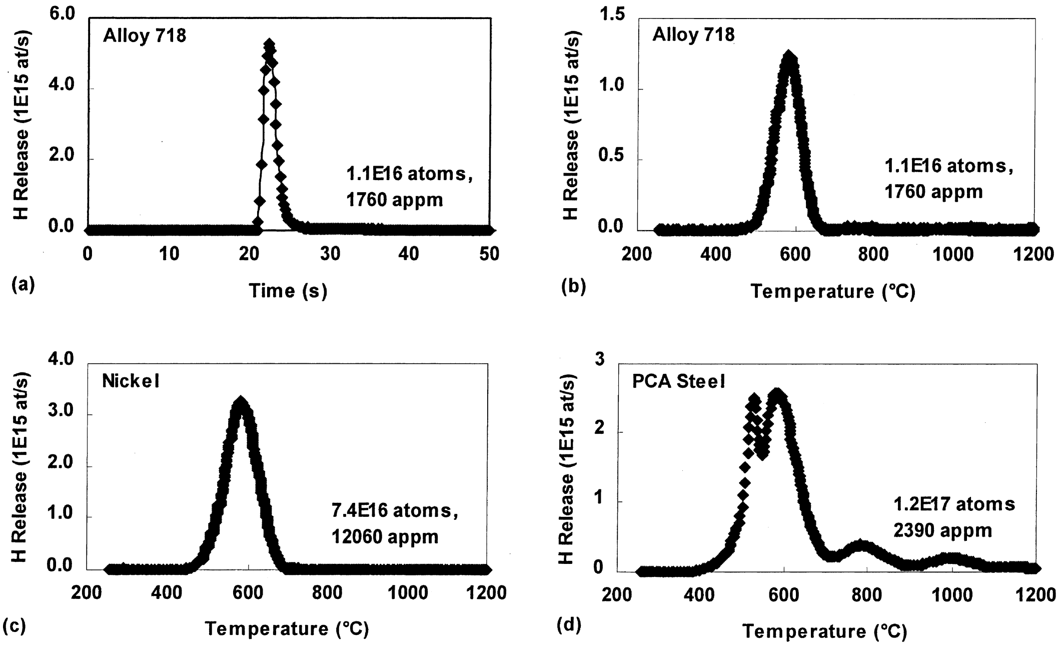

Fig. 3. Hydrogen release curves for Inconel 718 (a, b), nickel (c) and PCA steel (d). Curve (a) is versus time (s), curves (b)–(d) are versus temperature (°C).

nickel released hydrogen in single narrow peaks, the PCA steel showed four separate releases, suggesting that more than one trapping site is operating.

Fig. 4 shows the hydrogen release curve as a function of temperature for a ~9 mg sample of powder metallurgy tungsten from the APT program, irradiated to ~9 dpa at ~50°C. Similar to the PCA steel, there are four well-defined and separate releases, again suggesting trapping of the hydrogen is occurring at very different types of sites in the tungsten matrix. The total integrated hydrogen release for this sample was ~4.2×10^{16} atoms, or ~1400 appm.

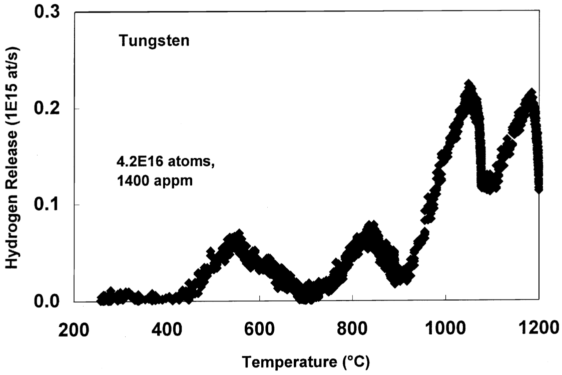

Fig. 4. Hydrogen release versus temperature for tungsten irradiated to ~9 dpa and ~50°C.

The system is currently being modified to provide computer control of the ramp rate such that activation energies associated with the various traps can be identified.

7. Conclusions

An analysis system has been developed to measure the hydrogen content of very small samples of irradiated materials from ~1 to many thousands of appm, with an estimated absolute uncertainty of ~20%. The sensitivity of the system is at least several orders of magnitude higher than currently available commercial systems, allowing analysis of much smaller radioactive samples, thereby significantly reducing safety concerns. Sample sizes ranging from ~0.3 mg to several hundred milligrams can be analyzed. The linearity of the system has been verified up to a total hydrogen release of at least 10^{17} atoms. When operated in a ramped temperature mode, the presence of multiple trapping sites for hydrogen can be identified using this technique and facility.

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