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Technique for Production of Calibrated Metal Hydride Films

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Abstract

A technique has been developed for producing calibrated metal hydride films for use in the measurement of high-energy (5-15 MeV) particle reaction cross sections for hydrogen and helium isotopes on hydrogen isotopes. Absolute concentrations of various hydrogen isotopes in the film is expected to be determined to better than $\pm 2\%$ leading to the capacity of accurately measuring various reaction cross sections. Hydrogen isotope concentrations from near 100% to 5% can be made accurately and reproducibly. This is accomplished with the use of high accuracy pressure measurements coupled with high accuracy mass spectrometric measurements of each constituent partial pressure of the gas mixture during loading of the metal occluder films. Various techniques are used to verify the amount of metal present as well as the amount of hydrogen isotopes; high energy ion scattering analysis, PV measurements before, during and after loading, and thermal desorption/mass spectrometry measurements. The most appropriate metal to use for the occluder film appears to be titanium but other occluder metals are also being considered. Calibrated gas ratio samples, previously prepared, are used for the loading gas. Deviations from this calibrated gas ratio are measured using mass spectrometry during and after the loading process thereby determining the loading of the various hydrogen isotopes. These techniques are discussed and pertinent issues presented.

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I. Introduction

A need exists for accurately measuring the concentration and depth profile of hydrogen isotopes in materials. A recent work (1) has shown that a technique has been devised and has been demonstrated to perform absolute quantitative measurement of hydrogen isotopes and to depth profile each isotope in solid material. In order to perform these measurements with high accuracy, the necessary scattering and reaction cross sections must be accurately measured.

Previous measurements of some of these cross sections have used gas targets where the absolute amount of H, D, and T were determined by the path length in the gas cell and the partial pressure of the hydrogen isotopes. The entrance and exit foils of the gas cell were, of necessity, thin to allow easy passage of the ions through the gas cell, i.e. low energy loss of the incident ions. In light of present day safety and environmental concerns this type of arrangement is not acceptable because of the possible rupture of a foil with the resulting contamination of the accelerator system and possibly the laboratory environment. With these considerations in mind we have designed an experimental arrangement which will allow the production of metal hydride films with a known amount of hydrogen isotopes in the film. This will allow accurate measurement of the cross sections and provide standards for use in various diagnostic apparatuses.

II. Technique for formation of metal hydride samples

This section provides a short description of the proposed technique to serve as a guide for the following information. Metal hydride films have been made and used for many applications for

many years but there has been little effort to produce these films with very accurate absolute amounts of H, D, and T in the film. The proposed technique is certainly not a new idea but is one that makes use of the many experimental and diagnostic facilities at Sandia National Laboratories. The basic idea is to deposit a metal occluder film of a particular thickness and then to subsequently load it with a known gas composition. In general, this is fairly simple but in practice this can be complicated by many factors if the uncertainty in the results is to be low, i.e. less than $\pm 1\%$.

Initially, a gas sample is prepared to NIST standards with the hydrogen isotope ratios specified as those that are desired. The metal occluder film is inserted into a carefully cleaned and conditioned loading chamber. The amount of the gas standard needed to load the metal occluder film is estimated; twice this amount is moved into the aliquot volume. This amount is accurately measured with the precision capacitance manometer (4) and the hydrogen isotope concentration ratios are analyzed with the precision mass spectrometer (5). This gas is then introduced into the loading chamber and the pressure and isotope ratio is again measured. The sample is heated to a temperature appropriate for the loading of the gas into the sample. After the gas has been loaded into the sample, the gas pressure is again measured and the ratio of the hydrogen isotopes remaining in the gas phase is analyzed. Using this data, the absolute amounts of the various hydrogen isotopes in the metal occluder film is accurately determined. There are many potential pitfalls to this simple approach and the most obvious ones are addressed in the next section.

III. Important concerns

One of the most important issues in the making of metal hydride films is the problem involving oxidation of the metal occluder film surface and the occluder/substrate interface. Another important issue is the measurement of the hydrogen isotope uptake in the occluder film. This involves: 1) measurement of the ratio of the hydrogen isotope concentration in the original gas sample used for loading the film, 2) different diffusion coefficients of the various hydrogen isotopes in the occluder film, 3) absorption and adsorption of the hydrogen isotopes on the walls of the loading chamber and its internal components, and 4) introduction of hydrogen into the gas phase from hydrogen diffusing in the chamber wall material and subsequently desorbing from the chamber walls and internal components.

The issue of surface oxidation of the metal occluder film is addressed via two avenues: 1) minimizing the exposure time of the film after evaporation to oxygen containing molecules and 2) deposition of a cadmium protective layer over the metal occluder film to preclude oxidation during any atmospheric exposure. (This suggestion was made by one of the authors: LB). This is more fully discussed in a later section.

IV. Design of the experiment

A loading chamber and associated tubing has been developed using purchasable equipment where possible. In order to reduce hydrogen loss from the chamber walls, tubing and valves, a passivation treatment of these surfaces has been accomplished. Previous studies (2) have lead to the processing of these surfaces using a proprietary treatment that has proven successful in previous loading and analysis systems (3). A schematic of the loading chamber is shown in Fig.

1. For this design, the internal surface area has been minimized while allowing attachment of the needed diagnostics and pumping system. A schematic of the loading system is shown in Fig. 2.

The holder for the metal occluder film sample is designed for both resistive heating and heating by IR radiation; sample heating may prove necessary to enhance the uptake of hydrogen by breakup of any surface oxide layer.

The pressure measuring system is a sensitive calibrated capacitance manometer with a dynamic range of 10^6 and with an upper pressure limit of 1 Torr (4). The hydrogen isotope analysis system is a 90° magnetic sector mass spectrometer, see Fig. 3, with a wide dynamic range (10^9) and which is linear over a broad range, i.e. 10^{-10} moles to 10^{-6} moles, see Fig. 4 (5). The mass spectrometer was designed for high precision gas analysis and high accuracy isotope concentration and isotope ratio measurements for H, D and T. Comparison of results from the mass spectrometer with known hydrogen gas samples have shown that the uncertainty in the measurement is less than $\pm 1.9\%$ (3σ). The mass resolution varies from 300 to 5000 and the mass range is from 1 to 300. The entrance aperture is made from gold foil and maintains a controlled conductance.

The volumes of all the various parts of the loading system are determined using PVT measurements based on a known calibrated volume. These volumes can be determined with an uncertainty of less than $\pm 0.2\%$.

V. Gas loading procedure

The gas loading procedure is to mount the metal occluder sample in the chamber shown in Fig.

1. A schematic of the loading system is shown in Fig. 2. An amount of gas, about equal to twice the amount calculated needed to load the sample, is transferred from the gas standard to the aliquot volume. This gas pressure is measured and then analyzed using the mass spectrometer. Then the aliquot volume is opened to the loading chamber and the gas pressure is measured and analyzed using the mass spectrometer. For the case of a sample with cadmium overlayer, the cadmium layer is evaporated from the metal occluder film and loading is then accomplished with mild heating of the sample. After completion of the loading, the pressure of the remaining gas and analysis of the isotope ratio is made and the hydrogen isotope content of the metal film is determined.

It will be necessary to study various aspects of the loading process to determine what effects each step in the loading has on the final gas quantity retained in the metal occluder film and the isotope ratios.

VI. Prognosis and conclusions

All necessary components for the loading system are in hand and the passivation process is being performed on all vacuum components (2). All diagnostics are available and calibrated. The system will be assembled, tested and conditioned before any loading of samples. It is anticipated that calibrated samples will be made by the end of the first quarter of 2000. Using this procedure

and the analysis techniques described in Ref. 1, samples with various thicknesses and different loading ratios can be made on demand with an uncertainty of about 1%.

1. James F. Browning, Robert A. Langley, Barney L. Doyle, James C. Banks, and William R. Wampler, to be published in Nucl. Instr. Meth. B (March 2000).
2. The surface treatment is proprietary and is performed by Tek-Vac Industries Inc., 172-176 Expressway Drive So., Brentwood, NY 11717.
3. There exist results of previous surface conditioning studies, both classified and unclassified, which deal extensively with this subject matter but is mainly in reports. For information on the source and contents of the reports contact the first author.
4. Capacitance Manometer, 1 Torr Head, MKS Baratron, Six Shattuck Road, Andover, MA 01810.
5. Mass spectrometer (MAT 271 HDT), Finnigan, Bremen, Germany.

Fig. 1 Load chamber design

Fig. 2 Block diagram of loading system

Fig. 3 Geometry of MAT 271 HDT

Fig. 4 Mass spectrometer response to molar input of hydrogen

Load Chamber Design

Block diagram of loading system

Geometry of MAT 271