ABSTRACT

The commonly available techniques for the determination of hydrogen dissolved in solids are usually destructive from the point of view of the sample. A new, nondestructive method for this kind of measurements has been developed at our laboratory, with the requirement of improved sensitivity for massive samples. This scattering method is based on the use of epithermal neutrons, and has been implemented through the design and construction of a spectrometer dedicated to that task. In addition, the traditional transmission method has been employed to determine hydrogen content in metals, using the full subthermal and thermal neutron energy ranges; in certain cases, this kind of measurements is able to produce integral information about the dynamics of the proton in the metal lattice. A pulsed neutron source based on an electron LINAC is employed, together with time-of-flight techniques. In this work we will present some results illustrative of the sensitivity achieved by these neutron techniques.

I. INTRODUCTION

The problem of hydrogen content and diffusion coefficient determinations in metallic systems has been explored in the past using different nuclear techniques, especially by thermal neutron scattering [1,2]. In this work we discuss the basic ideas and present the results obtained with the application of two non-destructive methods based on neutron techniques, aimed at the determination of hydrogen content in metals for the whole range of hydrogen concentration. Such determinations require a high degree of accuracy in the cross sections involved, and this in turn demands a detailed study of the models which represent the neutron-atom interaction in metal-hydrogen systems.

The first method is based on transmission measurements over the thermal and subthermal neutron energy range, exploiting the fact that the hydrogen scattering cross section is one order of magnitude larger than that of almost any other nuclei. This fact is especially valid at very low incident neutron energies, where the significant elastic coherent component - revealing the crystalline structure of the solid - does not exist. Although in the past transmission experiments were performed to tackle this problem, the method discussed here is novel with respect to the energy range covered and the data analysis procedure employed [3]. We illustrate this method through experiments performed on Zircaloy IV samples with both low and high hydrogen contents.

The second method, based on neutron scattering, is completely new and exploits the large difference in energy-transfer between the neutron-M (M: metal) and neutron-H scattering processes. We will outline the conceptual aspects of this method, the calculations needed for the optimization of the experimental design, and present some preliminary results obtained on steel samples. A complete description of this method was given in [4].

II. BASIC CONCEPTS

In discussing the theoretical approach to the computation of hydrogen and metal cross-sections, two separate situations must be distinguished,

Hydrogen in solid solution. In the case of solid solutions of hydrogen located in interstitial sites in metals, when the hydrogen concentration is sufficiently low, each hydrogen can be considered in isolation in a metallic lattice that is altered only in the immediate vicinity of the hydrogen.

Even though from a macroscopic point of view hydrogen has a considerable mobility in most metal lattices at room temperature, at a microscopic level its dynamics is determined by a residence time in an interstitial site and a much shorter hopping time between neighbouring
interstitial sites. Therefore, from a neutronic point of view and for the thermal energy range, H can be thought as conforming a pseudomolecule MH. In such a system, the characteristic frequency spectrum of H consists of a high frequency component corresponding to the optical mode of vibration inside the interstitial potential, in addition to a low frequency component associated to the acoustic modes of the host lattice.

**High hydrogen concentrations.** When the hydrogen concentration is larger than the terminal solubility the system consists of two phases: the solid solution at the terminal solubility and the hydride with almost stoichiometric concentration. Because these two phases have different crystalline structures the metal cross-section has to be computed for each phase.

In the hydride the vibrations of the hydrogen can be described by an analysis in terms of lattice dynamics. As in the precedent case, if the mass of the metal is much greater than that of hydrogen, the frequencies of vibration will be described by acoustic and optical dispersion curves, with the hydrogen amplitudes small in the acoustic modes and large in the optic modes. In many systems [5] the only difference between the hydrogen frequency spectra corresponding to the hydride and the solid solution consists of a small variation in the oscillation frequency of the optic modes.

**III. CROSS-SECTIONS CALCULATIONS**

**Cross sections of crystalline solids.** A complete derivation of the relevant formulas describing the interaction of thermal neutrons with crystalline solids is given in many textbooks (see e.g. [6]). The evaluation of the different components of the total cross section was performed with the computer codes CRIPO [7,8] and XTAL[9], which use a Debye model to represent the phonon spectrum of the solid, and a mass expansion for the total incoherent cross section. We show in Fig.1 our calculated total scattering cross section of Zr over the thermal energy range.

**Cross sections of hydrogen.** We have used a synthetic scattering function (SSF) developed by us [10], to represent the scattering law of H in the host metal lattice using the frequency spectrum given in [11]. The main advantages of the SSF are its flexibility to describe - in the incoherent approximation - the interaction of slow-neutrons with molecules, and the analytic character of the resultant expressions for scattering kernels and total cross sections. A full description of the model is given in the above references, and we must only emphasize here that it has been successfully applied to different problems in neutron and reactor physics. The total cross section of H in ZrH obtained from the SSF is shown in Fig. 1 compared with the experimental data presented in the next section.

**IV. TRANSMISSION METHOD**

Once the contributions to the total cross section due to the metal lattice and the hydrogen dissolved in it can be calculated in a reliable and accurate way, a transmission experiment performed over the full thermal energy range is able to yield the hydrogen content in the sample system. The typical behaviour of those contributions (see Fig.1) indicate that an iterative procedure can be used, where the data over the epithermal, 'free-atom' region, are fitted to extract the effective number of metal scatterers in the sample, while the subthermal region is most sensitive to the hydrogen contribution. In this manner, self-consistent values of the metal- and hydrogen- atom number densities can be obtained.

**Low hydrogen content.** We performed a transmission experiment, with neutron energies from 0.0008 eV up to 10 eV, on a Zircaloy-IV sample for which a full compositional analysis was available.
The low-energy cross section data are shown in Fig. 2-(a) compared with the evaluated curve (b) for pure Zry. The ratio NH/NZr obtained according to the fitting procedure described above is shown in Fig. 2-(c), giving a value of (39±3) wt ppm of H for this sample.

**High hydrogen content.** A highly hydrided Zircaloy-IV sample was prepared by direct absorption from the gas phase at 400°C and at a pressure of 40 atm. A transmission experiment was carried out and the relative concentration of each phase was determined by the same iterative procedure used in the low concentration case. From the fitted parameters the sample consists of 78% hydride and 22% pure Zircaloy.

We can use this transmission measurement to isolate the hydrogen contribution to the total cross-section over the whole energy range covered by the experiment. This is shown in Fig. 3 where the oscillations present in the cross-section are due to the highly defined oscillation frequency of the optic modes [12]. In contrast, we also show the results obtained for hydrogen in magnesium hydride where no oscillations are observed. This fact can be explained considering that Mg is lighter than Zr, so the acoustic and optic modes are no longer fully decoupled.

![Figure 3 - Total cross-sections of hydrogen in Zircaloy-IV hydride and in Magnesium hydride.](image)

**V. SCATTERING METHOD**

Our new scattering method is based on a simple concept. An incident spectrum from a pulsed source is ‘marked’ by a notch filter, before hitting the sample. The scattered neutrons are detected by a bank placed at a certain scattering angle and flight-path (Figure 4). Neutrons that have been scattered by the metal atoms will essentially reproduce the incident spectrum, including the window produced by the filter, after suffering almost elastic interaction processes. On the other hand, those scattered by the hydrogen atoms present in the sample, will significantly change their energy in the laboratory system, and the emerging spectrum from these interactions will be rather different from the incident one, as seen in the time-of-flight (TOF) scale.

![Figure 4 - Schematic diagram of the experimental setup](image)

In the case of a real hydrogenated sample, incident neutrons with energies above that of the filter's resonance energy, which reach the sample before the 'resonance' energy (non-existent) neutrons, can be scattered by hydrogen atoms, loose energy in this interaction, and due to their reduced velocity upon leaving the sample, employ enough travel time to arrive at the detector within the time window blanked by the resonance filter. Therefore, the spectrum window will become ‘contaminated’ by those hydrogen-scattered neutrons, giving rise to an enhanced signal to noise ratio over that portion of the TOF scale.

![Figure 5 - TOF spectra for neutron scattered by H and Zr.](image)
alone, are shown in Fig.6-(b). It must be emphasized that the region of interest to compare the spectra is that around the window generated by the In filter as shown in Fig 6-(a), and this in turn demands a careful background measurement to reduce systematic errors as the non vanishing intercept of the fitted line at zero H content observed in Fig. 6-(b).

VI. CONCLUSIONS

We have shown that thermal neutron transmission experiments, in combination with accurate evaluations of the relevant total cross sections, can be used as a fast, non-destructive way to determine hydrogen contents in solid systems. Our proposed scattering method has been experimentally validated, and its capability to measure and resolve very low hydrogen contents demonstrated. These methods can be advantageously used in the cases of radioactive samples, where handling could be a problem in the traditional procedures.

In addition, we indicated the capabilities of the transmission method to obtain integral information about the dynamics of hydrogen in metal lattices over a wide energy range. We believe that this method could be very fruitful to study the relative weights of the acoustic and optic modes in the hydrogen frequency spectra for systems where only incomplete information is available. The complete formalism to tackle this problem and other experimental details will be described in a forthcoming publication.