ToF-SIMS and ERDA study of hydrogen and deuterium in nickel-base alloys oxidized in water

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ABSTRACT

The depth profiling of hydrogen and deuterium in polycrystalline and monocrystalline Nickel-base alloys (Ni-16Cr-8Fe, wt%) was performed by Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and Elastic Recoil Detection Analysis (ERDA) after oxidation in simulated primary medium conditions containing 9 at.% D_2O. The use of deuterium isotopic tracer in ToF-SIMS has demonstrated the presence of deuterium in the oxide layer for oxidation times of 300 min and 100 h. The quantities of deuterium were determined by ERDA using a 2 MeV ^4He ion beam. Finally, the penetration coefficient α was calculated, and ranged from 0.01 to 0.04.

1. Introduction

Absorption of hydrogen in the near surface region of solid materials is a major issue in several applications of metallic materials. Hydrogen embrittlement is usually understood as the unwanted delayed brittleness of a material which is caused by the presence of hydrogen within the material. Practically all metal materials can be damaged by the absorption of hydrogen, if a sufficient quantity can penetrate into the material [1].

Hydrogen, in its molecular form, is too large to diffuse interstitially in most metals, neither can it readily cross the gas/metal interface in the molecular form. So when materials are exposed to hydrogen containing substances such as water, H_2, etc., the molecule will firstly dissociate to give a hydrogen atom which is adsorbed at the metal surface [2]. The adsorbed hydrogen can then enter the material (absorption). After absorption, hydrogen can diffuse through interstitial sites, dislocations, and grain boundaries; it can react with lattice atoms to form hydride phases [3], which are considered to be one possible cause of hydrogen embrittlement due to their stability even at room temperature [4]. The effect of hydrogen on the corrosion of nickel-base alloys has been investigated previously [5–8]. It has been shown that hydrogen can enhance the dissolution of the alloy by favouring the dissolution of chromium. When the alloys are immersed in high temperature water, the water molecule dissociates to give hydrogen atoms which adsorb on the alloy during the formation of passive films, and the amount of hydrogen dissolved in water has an influence on the oxidation of the alloy. The detection and depth profiling of hydrogen isotopes is also very important for fusion reactor technology, for example. However, due to the difficulty in the detection of surface hydrogen by conventional methods, absolute coverage information is usually lacking.

Some papers dealing with hydrogen depth profiling using SIMS have been published [9,10]. It was found that hydrogen can diffuse through the oxide scales formed on Nickel base alloys, and interacts with point defects created by Ni^+ implantation. It has also been shown (by TDS) that the diffusion of hydrogen is influenced by grain boundaries [11]. However, one of the most important limitations of ToF-SIMS is that due to a large variation of ionization probabilities among different materials, it is considered to be qualitative, with quantification only possible using specific standards for each given matrix.

ERDA [12], also referred to as forward recoil scattering, is an ion beam analysis technique used in materials science to obtain elemental concentration and depth profiles in thin films [13,14]. ERDA has proved to be effective in the quantification of hydrogen [15]. When applied with a ^4He ion beam of MeV energy, the three stable hydrogen isotopes H, ^2D and ^3T can be depth profiled simultaneously, with less target damage as compared with the use of higher-Z analysing beam [16,17]. Absolute determination of ^1H and ^2H content by ERDA is matrix-independent and needs only a stable standard, with a known content of these atoms.

In this work, hydrogen incorporation during the oxidation of Ni based alloys under conditions simulating operating conditions of the

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PWRs is studied. Use of isotopically labelled water, enriched in deuterium, provides clear evidence of the origin of the hydrogen in the oxide and the underlying alloy, and allows discrimination from hydrogen of natural isotopic composition that may be present on the surface of the samples after exposure to air. TOF-SIMS provides well-resolved concentration depth profiles, whilst ERDA with a He incident beam is used to provide absolute quantification.

2. Material and methods

Two types of NiCrFe alloys were used in this work: cast polycrystalline alloy (Ni-16Cr-9Fe (wt%)), (referenced WF675), provided by the company Imphy, and monocrystalline (110) and (111) alloys (Ni-16Cr-8Fe (wt%)), provided by the Siberian Physical-Technical Institute (Laboratory of Physics of High Resistance Crystals). The samples are plates with surface area of 1.1×1.1 cm^2 and thickness of 1 mm. They have been oxidized in water at high pressure and high temperature (155 bar, 325 °C), containing 9 at.% D_2O, for different oxidation times (1 min, 300 min, 100 h), in the titanium loop of a recirculating autoclave simulating chemical and thermal conditions of the primary circuit of PWRs.

In the present work, ToF-SIMS is applied at first for the qualitative analysis of hydrogen depth profiles. For ToF-SIMS, a solid sample surface is bombarded with a pulsed primary ion beam. The sputtering angle is kept constant (45°). Possible oxide and/or metal crystallographic orientation effects on sputtering rate are not taken into account. Both atomic and molecular ions (secondary ions) are emitted from the outer layers of the surface and extracted. Their mass/charge ratio is measured by their time of flight to the detector. As with most of the surface sensitive techniques (XPS, LEIS/ISS, AES…), ToF-SIMS requires ultra-high vacuum (UHV) in order to protect the surface from contamination, and to limit the interaction between the produced secondary ions and the environment that could lead to a drastic decrease of the secondary ion intensity.

The measurements were performed using a ToF-SIMS V spectrometer (ION-TOF GmbH, Muenster, Germany). The normal operating pressure in the main chamber was less than 5.0×10^{-9} mbar. A Bi$^+$ primary ion beam with a current of 0.2 pA was used to scan over an area of 100×100 μm^2 for the analysis. In order to measure the composition depth profile, a dual-beam mode was used and the analysis was performed alternately with a sputtering step using a 29 nA (500 eV) Cs$^+$ ion beam, rastered over an area of 500×500 μm^2 for polycrystalline alloy sample oxidized in high temperature water for 1 min and 300 min, and 300×300 μm^2 for polycrystalline alloy sample oxidized in high temperature water for 100 h and monocrystalline alloy samples.

In ToF-SIMS depth profiles, the intensities are usually plotted as a function of sputtering time. The calibration to oxide layer thickness was performed with a mechanical profilometer (Dektak 150, Veeco, Veeco-Instrument Europe, Dourdan, France), which measures independently the thickness of the depth profiles. The deduced sputtering rates were 0.014 nm s^{-1} for a sputtering area of 500×500 μm^2, and 0.040 nm s^{-1} for 300×300 μm^2.

ERDA, using a ∼2 MeV beam of ^{4}He in the Fast Ion Beam Analysis System (SAFIR) platform of the Pierre and Marie Curie University (UPMC) was then performed for the quantitative analysis of hydrogen. The experimental arrangement employed for the measurements is shown schematically in Fig. 1. The energetic alpha particle beam is directed onto the sample to be characterized and (as in Rutherford backscattering, RBS) undergoes elastic collisions with the nuclei of the target atoms. The energy spectrum of the atoms recoiled from the target by the incident particle is measured with a 300 mm^2 silicon particle detector, and a 15×1 mm^2 collimator in front to limit kinematic broadening of the spectrum. A Mylar absorber foil of thickness (6 μm) sufficient to prevent elastically scattered primary beam and higher mass recoils from reaching the detector, but sufficiently thin to allow the recoiled hydrogen and deuterium nuclei through, is placed in front of
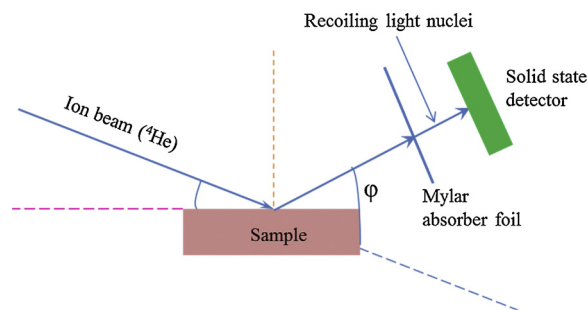

Fig. 1. Scheme of ERDA experimental device.

the detector. The samples and detector are in a chamber with vacuum of 10^{-6} mbar.

Turos and Meyer [18] have studied the influence of scattering angle on the sensitivity of the measurement, and concluded that $\varphi \approx 30°$ is the optimum scattering angle to have an appropriate recoil energy and cross section for the measurement, so in this study, the position of the detector was adjusted to have a scattering angle of about 30°. In this geometry, the incident beam enters the sample, and the recoils leave the sample, at 75° from the surface normal. The solid angle of the detector is about 2×10^{-3} sr. Typically a beam of about 40 nA collimating to a diameter of about 5 mm was used, with incident beam fluences up to 2.5×10^{16} He/cm^2. We verified that up to such fluences, the D and H content was stable under the beam.

Standard samples of polyethylene $(C_8H_8)_n$ spin-coated into silicon wafers were used for the calibration of energy and quantification of hydrogen, with the quantity of hydrogen in the polymer films deduced from nuclear reaction analysis (NRA) [19] of the carbon via the ^{12}C(d, p_0)^{13}C reaction [20]. Oxygen areal density in the oxidized samples was determined with NRA via the ^{16}O(d, p_1)^{17}O reaction using anodic Ta_2O_5 reference samples [21].

3. Results and discussion

3.1. Characterization of oxide layer and hydrogen penetration by ToF-SIMS

ToF-SIMS was used in order to characterize the oxides formed on the Ni-based alloy and to detect the presence of hydrogen in the oxide layer and/or the alloy. Fig. 2 shows the ToF-SIMS profiles obtained on polycrystalline Ni-16Cr-9Fe (wt%) alloy.

Fig. 2(a) shows the characteristic ToF-SIMS profiles obtained on the polycrystalline alloy oxidized for 1 min in H_2O + 9 at.% D_2O at 325 °C. We can see from these ToF-SIMS profiles that, after 1 min of oxidation, the oxide layer is duplex with an outer layer rich in nickel and iron, highly hydrated as indicated by the OH$^-$ and OD$^-$ signals and an inner layer rich in chromium. The OD$^-$ signal decreases very quickly after the M/O interface, while the OH$^-$ remains relatively intense. It is observed that after 1 min of oxidation, the NiCrO$^-$ signal reaches its maximum intensity in the inner oxide layer, close to the M/O interface. The presence of this signal indicates that the inner chromium-rich oxide contains islands of nickel chromite ($NiCr_2O_4$).

After the characterization of the oxide layer, the signal of deuterium was analysed. As we can see from Fig. 2(a), the D$^-$ signal decreases gradually as we go into the oxide layer, and falling to zero in the inner oxide layer. The D$^-$ signal decreases faster than other characteristic signals of the oxides, so we could conclude that for the sample oxidized in deuterated water for 1 min, deuterium did not enter the metallic substrate, and there is no hydrogen penetration into the metallic alloy.

For the sample oxidized for 300 min in deuterated water as shown in Fig. 2(b), the oxide layer is also duplex, with an outer layer (extending from 0 to 16 s), rich in nickel and iron oxide, highly hydrated as indicated by the OH$^-$ and OD$^-$ signals. An inner layer rich in chromium oxide is observed, with the presence of islands of $NiCr_2O_4$ close to the