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Hydrogen loss during N-15 nuclear reaction analysis of high strength steel

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ABSTRACT

High strength steel samples were analysed by N-15 nuclear reaction analysis in order to detect hydrogen that may have been introduced by electroplating process. The NRA signal decreased during exposure of the ion beam and residual gas analysis showed that the gas was desorbed by the beam interaction. The variable hydrogen signal could be well described as the sum of a constant concentration and a fraction susceptible to second order desorption. A mechanically polished bevel allowed measurements to be extended to a depth of 0.2 mm.

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1. Introduction

High-strength steels are particularly sensitive to embrittlement by hydrogen: when hydrogen penetrates the steel in only small concentrations, its mechanical properties are negatively affected [1]. In order to protect the steel parts from the intrusion of hydrogen during its lifetime, steel parts are often protected with an anti-corrosion coating. However, since this coating is often electrochemically deposited ("plating"), hydrogen can also be introduced at this time [2]. It is therefore important to understand and characterize the hydrogen content of high-strength steels after the plating process.

A well-known method for accurately measuring the hydrogen concentration depth profile is nuclear reaction analysis (NRA) using an N-15 beam [3,4]. However, during a NRA measurement the signal may decrease due to beam-induced loss of hydrogen from the sample, an effect that has been observed in semiconductors [5–7] and steel [8]. In this work, we study the hydrogen loss mechanism during NRA analysis and show that reliable depth profiles can be obtained in spite of the hydrogen loss.

2. Experimental details

The samples were made with a high strength martensitic steel (type 4340). The steel was initially electrochemically plated with a cadmium coating. This coating is regularly used in industry even though the plating is susceptible to introduce hydrogen into the steel. Fig. 1a shows a scanning electron microscopy image of the surface of the sample; it can be seen that the plating is several tens of microns thick and very irregular. Before ion beam analysis, the plating was chemically removed to make it possible to measure the concentration of hydrogen in the steel. Fig. 1b is an image taken after removing the Cd layer. The image shows the presence of considerable surface roughness.

The concentration of hydrogen was evaluated by the $^{1}H(^{15}N,\alpha\gamma)^{12}C$ nuclear reaction. By varying the energy beyond the resonance value of 6.385 MeV, it was possible to produce a profile of the concentration as a function of depth. The size of the beam is typically 2×7 mm^2 and the 4.43 MeV gamma radiation emitted by the nuclear reaction was captured by a bismuth germanate ($Bi_4Ge_3O_{12}$) scintillator. The N^{2+} beam was produced with a current under 25 nA at a 6 MV Tandem particle accelerator. The intensity calibration was performed with a sample of diamond-like carbon (DLC) with a known and uniform hydrogen concentration (11.5 at.% previously evaluated by RBS). No significant hydrogen loss was observed during the DLC calibration measurements when cooled with liquid nitrogen.

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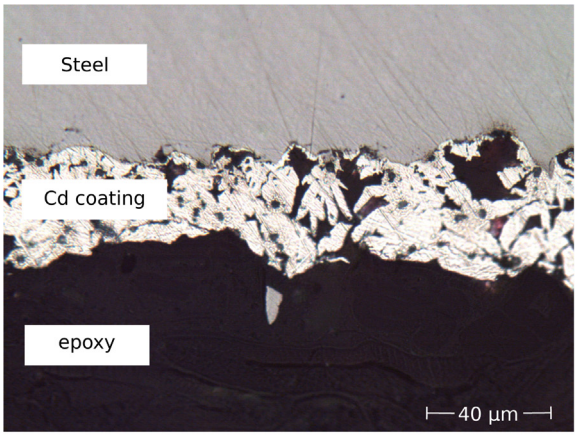
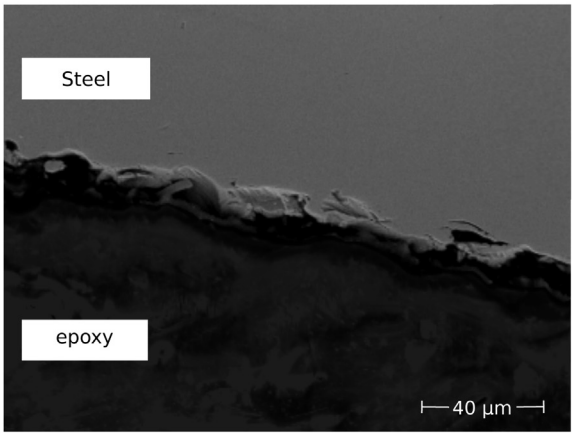


(a)



(b)

Fig. 1. SEM picture of a plated steel (a) and a plated steel that has been stripped (b).

3. Hydrogen loss characteristics

During an NRA measurement the high energy ions can provoke hydrogen loss as shown in Fig. 2. This figure shows the number of gamma counts as a function of integrated charge on the sample, using 6.5 MeV N-15 ions for which the resonance occurs at a depth of about 33 nm. The black circles were taken at room temperature, while the blue triangles was taken while the sample was cooled with liquid nitrogen. In both cases, it is obvious that the signal decreases significantly. For lower temperatures the loss of signal is slower and thus the temperature plays a part in the dynamics of the signal decay. At high fluences, the signal tends towards a constant value which is well distinguishable from the background noise. The dotted line in Fig. 2 is a second order fit to which a constant has been added. This suggests that the desorption only occurs after a H_2 molecule has formed that then diffuses out of the analyzed area. The hydrogen concentration remaining in the sample would be written as:

$$[H](\phi) = \frac{A}{1+\phi/\tau} + B \tag{1}$$

where $[H]$ is the concentration of hydrogen as a function of fluency, A the fraction of hydrogen concentration that is susceptible to desorption, ϕ the ion fluency or integrated charge, and τ a characteristic fluency. The constant B has been added which corresponds to the concentration of hydrogen that remains fixed (or desorbs at a much slower rate) in the sample even at high fluences. Based on visual inspection as well as χ^2-square criteria, second order fitting gave much better results than a single exponential decay did. Moreover, we compared the numerical values of the constant fraction for two fitting methods (first and second order) and the values are shown in Table 1. When using a second order fit, the fraction of hydrogen remaining fixed in the sample appears independent of analysis temperature as one would expect whereas in the case of first order fitting very different values need to be used in order for the fit to work at smaller fluencies.

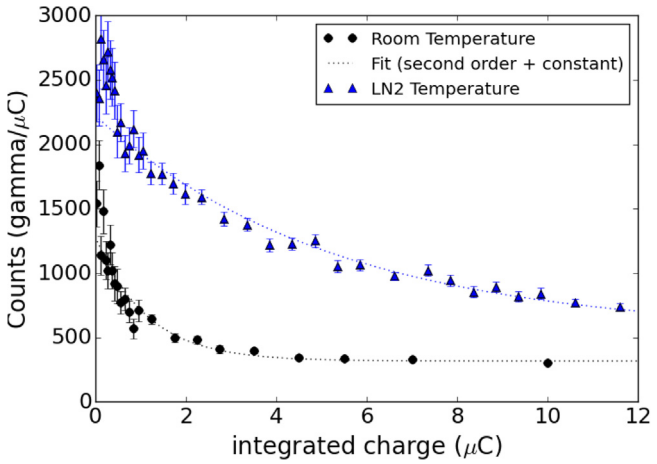


Fig. 2. NRA signal as a function of integrated beam charge with a beam of 6.5 MeV for a plated steel.

The desorbed gaseous hydrogen thus formed was directly measured by a residual gas analyzer as shown in Fig. 3. This is a measurement on a different vacuum chamber (allowing the RGA to be quickly hooked up) using an Si ion beam of similar depth penetration and beam current to the N-15 beam used for NRA. The data could again be described by second order desorption, but note that in this case the instantaneous hydrogen loss is measured and not the amount of hydrogen remaining in the sample. Thus the derivative of Eq. 1 was used to fit the data. The hydrogen desorption measured by RGA at different target temperatures shows the same tendency as found for the hydrogen concentration measured by NRA.

By changing the energy of the beam, it is possible to analyze the samples at different depths. Thus, for ions of lower incident energy, more energy will be deposited near the surface whereas higher energy ions would probe a thicker layer. Fig. 4 shows RGA measurements made by using silicon ions at two different energies. The blue line showing the largest signal comes from a 3 MeV Si^{2+} beam, while the red line (middle curve) comes from a 12 MeV ion beam measuring a fresh spot on the same sample. Since the signal is much higher at 3 MeV one concludes that the hydrogen desorption occurs primarily from the surface. When a measurement is made at 12 MeV at a location already analyzed at 3 MeV (green line) only a very weak signal is observed. This confirms that hydrogen is desorbed from the surface: by increasing the energy, the ions reach a deeper region of the sample but since the signal does not increase, no hydrogen appears to desorb from deeper layers.

Table 1
Comparison of the fit constant between first and second order desorption.

First order	Room temperature	$317 \pm 7\,\gamma/\mu C$
	Cooled	$535 \pm 10\,\gamma/\mu C$
Second order	Room temperature	$248 \pm 10\,\gamma/\mu C$
	Cooled	$259 \pm 20\,\gamma/\mu C$

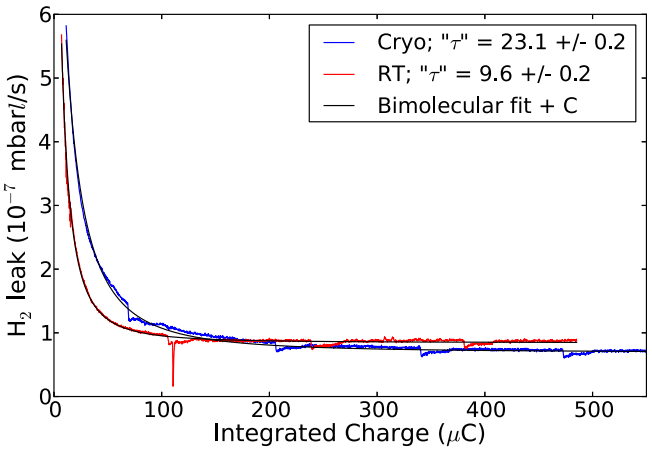


Fig. 3. Desorption of hydrogen for a plated steel at different temperatures.

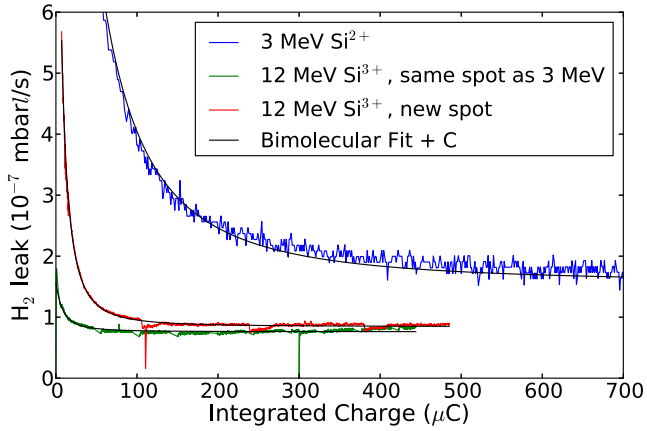


Fig. 4. Desorption of hydrogen for different energies.

4. Hydrogen depth profile near the surface and beyond

In spite of the loss of signal during an NRA measurement, it is possible to evaluate the hydrogen concentration as a function of depth by using the constant, fixed, fraction as determined by the second order fit. Unfortunately, NRA does not allow for analysis beyond 2 micrometer in steel so a mechanically machined bevel was used to reach greater depths. The bevel was made by polishing away some of the surface, proceeding slowly so as to avoid modifying the surface composition. The depth profile of the machined surface measured by stylus profilometry is shown in Fig. 5 as a black curve. The horizontal (unpolished) and sloped (polished) part of the profile were both described by a simple 2-order polynomial curve and the residuals, multiplied by a factor 20, are shown as separate curves (red and blue) near the top of the graph. The residuals on the polished part show that the surface roughness is much reduced and at a larger length scale after polishing. When measuring a polished area by 6.5 MeV NRA, the data can again be described by a second order fit but the hydrogen loss is much reduced compared to measurement on un-polished steel. Nevertheless, some loss still occurs and we suggest to use the constant (fixed) value extracted from the second order fit as a reliable measure of the hydrogen concentration just below the polished surface.

Fig. 6 shows the hydrogen concentration as a function of depth, deduced from the constant fraction extracted after fitting a curve of gamma counts as a function of ion fluency. Shallow points (less than 2 microns) were obtained by increasing the N-15 ion energy and hence the resonance depth whereas deeper points were

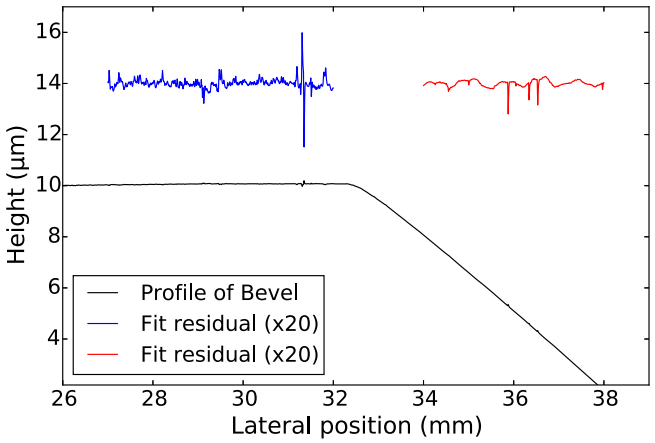


Fig. 5. Bevel profil and surface roughness of the steel sample.

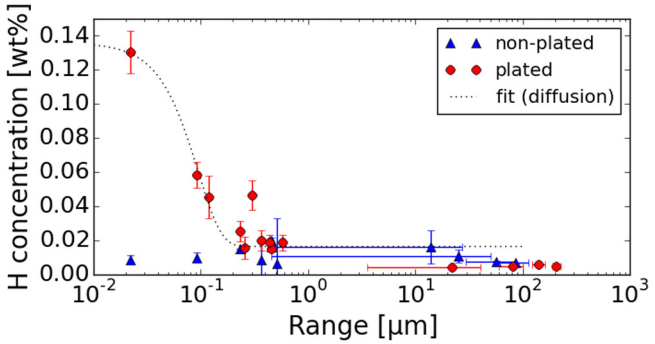


Fig. 6. Mass percent of hydrogen atoms as a function of depth.

obtained using 6.5 MeV N-15 incident at different locations on the beveled part of the sample. The data in red are taken with the sample that had been plated and stripped, while the data in blue is the data taken with a reference sample of the same steel that had never been plated.

The dotted line shown in Fig. 6 is a fit to the diffusion equation for a constant source at the surface with a diffusion length of 0.095 ± 0.012 micron.

5. Summary and conclusions

The hydrogen signal loss during a nuclear reaction analysis on a high-strength steel of type 4340 was studied. This hydrogen loss can be described by a second order desorption mechanism and is slowed down when cooled by liquid nitrogen. The desorption of hydrogen gas during ion beam irradiation was also detected by a residual gas analyzer. The desorbing hydrogen originates at or near the surface. Not all the hydrogen desorbs: the fit shows that a fraction remains or desorbs at a much slower rate. A mechanically polished bevel allowed the NRA technique to be used to probe well beyond a few microns and a concentration profile characteristic for diffusion from a constant source at the surface with a diffusion length of 0.095 ± 0.012 micron was found for a steel sample that has been plated and stripped. A reference steel sample did not show such a hydrogen profile.

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