Available online at www.sciencedirect.com

ScienceDirect

Applied Surface Science 253 (2006) 1150–1153

applied surface science

www.elsevier.com/locate/apsusc

H uptake kinetics of FeTi films coated with Ni

E.M.B. Heller [a], A.M. Vredenberg [a,*], D.O. Boerma [b]

[a] *Debye Institute, Surfaces, Interfaces and Devices, Universiteit Utrecht, P.O. Box 80.000, 3508 TA Utrecht, The Netherlands*
[b] *Centro de Micro-Análisis, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain*

Received 29 March 2005; received in revised form 12 January 2006; accepted 24 January 2006
Available online 24 February 2006

Abstract

The H_2 storage material FeTi can be fully charged through a Ni coating in the course of hours. A mild activation, either by long H_2 exposure at RT, or annealing in 35 mbar H_2 at 150 °C, leads to a full uptake in minutes. The enhancement of the uptake rate after activation is caused by a reduction of the Ni-oxide surface. Ni does not limit the hydrogen uptake rate once the surface is clean. However, the Ni surface is sensitive to contamination, as for instance by CO adsorbed from air.

PACS: 68.35 Fx; 81.05 Bx; 81.65 Mq; 89.30 xf

Keywords: FeTi; Ni; Hydrides; Hydrogen storage; Kinetics; Thin films; Energy storage

1. Introduction

FeTi is an inexpensive H_2 storage material, which takes up large amounts of H_2 [1]. However, an expensive activation treatment (at high temperature in either vacuum or high H_2 pressure) is necessary after air-exposure. During this activation treatment the surface oxide, which is not permeable for H_2, dissolves into Fe and TiO_2 [2]. At this activated surface H_2 can dissociate and H can be taken up in the material. An effective way to improve the corrosion resistance of FeTi is to cover the FeTi with a coating of a non-oxidizing, H_2 permeable material [3–5]. In previous research it was shown that a Pd coating protects FeTi against de-activation during exposure to air [6]. However, Pd is an expensive metal.

Nakamura et al. showed that besides Pd, also Ni and Fe coatings improve the H uptake kinetics of Ta wires [4]. This was confirmed by Uchida and Fromm for these coatings on Ti [7]. As is known from literature, Ni forms no hydride at RT below 6 kbar [8]. The initial sticking coefficient of H_2 is almost unity at RT. Dissociation occurs without an activation barrier, as in Pd [9,10]. Also, diffusion of H in Ni is fast: $D = 6.6 \times 10^{-10}$ cm^2/s at RT [11]. These properties make Ni a very suitable coating material. Because Ni is much cheaper than Pd, it is interesting to investigate the effectiveness of a Ni coating as a protective layer on FeTi. Since the H_2 absorption characteristics of our amorphous FeTi films were extensively discussed in another paper [6], in this article we focus on the kinetics of H uptake through a Ni coating before and after air-exposure.

2. Experimental

The H charging kinetics is studied on a FeTi/Ni sample structure. Thin films of FeTi were deposited on Si wafers by e-beam evaporation (at $p \sim 5\text{–}10^{-7}$ mbar). The Ni coating was deposited immediately after deposition of the FeTi. The FeTi layers had a thickness of ~140 nm and a composition of $Fe_{43}Ti_{57}$, as determined with Rutherford Backscattering Spectrometry (RBS; using a 2.5 MeV He beam). The Ni layers were ~20 nm thick.

The H uptake kinetics of the layers was measured at RT in our high pressure hydrogen reactor (HPHR). This is a device in which the H uptake is measured by the change in pressure difference between a reference volume and a small volume containing the sample, which is monitored using a differential pressure gauge (this method is discussed in detail in ref. [6]). In the analysis of the H uptake in FeTi/Ni we assume no uptake in the Ni layer, because Ni does not form a hydride below 6 kbar at RT [8]. After charging, the layers were discharged by annealing

---

* Corresponding author. Present address: Ecofys bv, Postbus 8408, 3503 RK Utrecht, The Netherlands. Tel.: +31 30 2534249, fax: +31 30 2543165.
E-mail address: A.M.Vredenberg@phys.uu.nl (A.M. Vredenberg).

0169-4332/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2006.01.054

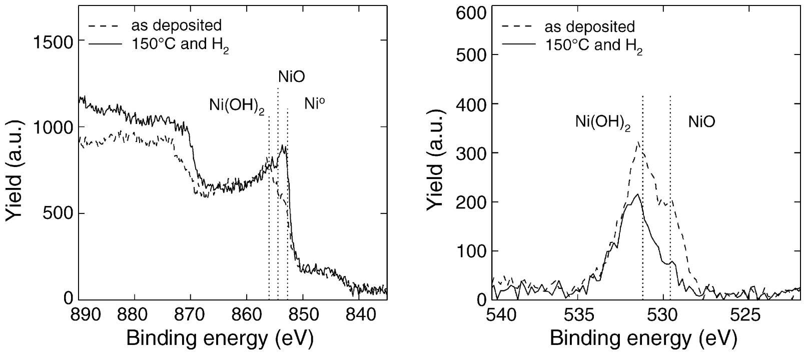

Fig. 1. XPS spectra of FeTi/Ni as-deposited, and after activation in 35 mbar at 150 °C and H charging in 800 mbar H_2 at RT. Left: Ni(2p); right: O(ls). The positions of the chemical states are indicated with dotted lines. In all cases the sample was exposed to air before the XPS spectra were taken.

to 150 °C in the HPHR, which was evacuated before the discharge. During discharging the pressure builds up to ~15 mbar H_2. From previous measurements it follows that a residue of H/M ~0.12 remains in the layer. Here H/M is the number of H atoms divided by the number of Ti + Fe atoms. The uptake data that we present in this paper are expressed as the difference in H/M, $\Delta H/M$, which equals zero at $t = 0$ (irrespective of the residue), and increases upon exposure to hydrogen.

Depth profiles of C and O were measured with elastic recoil detection (ERD) using a 66 or 72 MeV Ag beam and a δE-E telescope [12]. The 'bulk' contamination levels were below 0.5 at.%. After deposition, the H content was 0.015 H/M and 0.005 H/M in the FeTi and Ni, respectively. In as-deposited, air-exposed FeTi/Ni layers, O is present at the surface (8.5×10^{15} atoms/cm^2) and at the FeTi/Ni interface (0.7×10^{15} atoms/cm^2). C is present in quantities of 0.5×10^{15} atoms/cm^2 and 1.3×10^{15} atoms/cm^2 at the surface and the Ni/FeTi interface, respectively.

X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical state of the elements present in the first nanometers of the surface. XPS was performed using a CLAM-2 hemispherical sector analyzer and a Vacuum Generators XR2E2 Twin Anode X-ray Source employing a Mg K_α source to measure the Ni(2p), C(ls) and Fe(2p) peaks, and an Al K_α source to measure the Ti(2p) and O(ls) peaks. The source was chosen such that there was minimal overlap between the peaks. Spectra were analyzed by comparing the peak positions to literature data on chemical shifts [13]. XPS spectra of the Ni(2p) and O(ls) region of the as-deposited FeTi/Ni layer (see Fig. 1), showed that the Ni surface is partly oxidized. The position of the peaks points to the presence of Ni(OH)$_2$. No Fe or Ti signal was observed. From this we conclude that the Ni fully covers the FeTi layer.

3. Results and discussion

3.1. First H charging and activation treatment of FeTi/Ni

In the left panel of Fig. 2 the first charging of FeTi/Ni (in 800 mbar H_2 at RT) is shown. This sample had been exposed to air for a long time previous to charging. No H is taken up on a time scale of 60 min. Uptake does occur on a longer time scale, as is shown in the right panel of Fig. 2, which shows uptake curves for cycled layers which had been (re)exposed to air. When complete uptake has been reached during charging after air-exposure, the time needed for the next charging decreases from hours to minutes, i.e. to the value before exposure. This indicates that the surface reduces during the slow H uptake. This is in agreement with the rate difference after short (5 min) and long (2 days) air-exposure (see the right panel of Fig. 2), since one expects to grow a thicker oxide layer for longer air-exposure.

Since surface reduction seems necessary, a reduction of the surface in 35 mbar H_2 at 150 °C (for 30 min) was tried. As can be seen in the left panel of Fig. 2, there is H uptake of $\Delta H/M = 0.42$ during this treatment. Note the S-shape of the uptake curves, similar to the uptake curve after air-exposure. The shape of the curves seems analogous to the reduction of

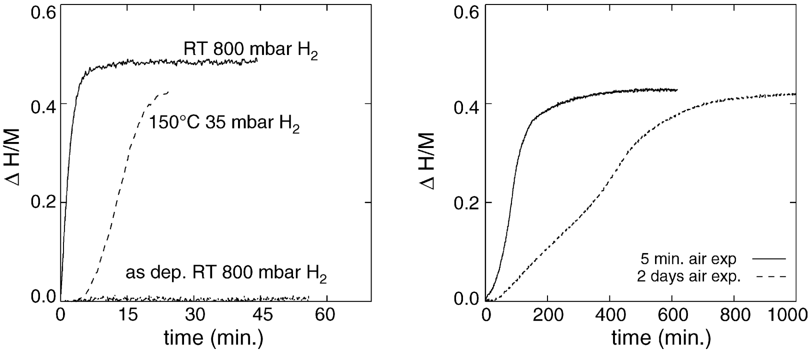

Fig. 2. HPHR uptake curves of FeTi/Ni in 800 mbar H_2 at RT. Right: uptake curves after air-exposure for 5 min (solid line) and 2 days, (dotted line). Before air-exposure this sample had been charged and discharged. Left: uptake curves of an as-deposited, air-exposed sample during the first charging; during subsequent activation in 35 mbar H_2 at 150 °C, and during the second charging.