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Deuterium thermal desorption from FeTi thin films

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Abstract

Iron–titanium thin films (FeTi) were deposited by r.f. magnetron sputtering on (100) oriented Si substrate and submitted to thermal annealing at 573 K in 10^6 Pa D_2 gas pressure to promote deuterium absorption. Sample characterization by X-ray diffraction spectroscopy (XRD) and conversion electron Mössbauer spectroscopy (CEMS) indicates that as-deposited and annealed samples have almost amorphous structure (a-FeTi). Thermal treatment in deuterium only induces the formation of metallic iron (α-Fe) precipitates in the near surface region of the sample. Thermal desorption spectroscopy (TDS) analysis shows a second-order desorption peak of deuterium at ~710 K with activation energy of 2.10 ± 0.05 eV. The desorption kinetics is controlled by deuterium recombination at the sample surface: the evaluated value of the activation energy indicates bonding of D atoms with sites in the surface oxide layer of the a-FeTi sample.
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Keywords: FeTi; Thin films; Hydrogen desorption kinetics

1. Introduction

The FeTi intermetallic compound is an important material for hydrogen storage because, in the form of metal hydride, it has about 2 wt.% gravimetric efficiency and, after activation, very fast absorption and desorption kinetics [1]. The study of hydrogen kinetics in FeTi thin film samples has provided important information on the surface processes leading to the activation of the material. Air-exposed FeTi surfaces are covered by a 10–30-nm thick layer composed of Fe–O and Ti–O mixed oxides [2], which has to be removed or made transparent to hydrogen by the activation procedure. This result is typically obtained by vacuum annealing at ~750 K followed by annealing in hydrogen atmosphere at pressures in the 10–50 atm range. X-ray photoelectron spectroscopy (XPS) analysis revealed that during the treatment the following phenomena occur: (a) the FeTi surface becomes Ti enriched (Fe:Ti=0.5), (b) surface Ti atoms are completely oxidized forming TiO_2 and (c) oxidized Fe atoms are reduced to metallic Fe precipitates with ferromagnetic character [3]. It is supposed that the surface activation is related to the presence of these transition metal precipitates where the H_2 molecular dissociation occurs [3]. Wulz and Fromm studied the passivation effect of the surface oxide layers on the hydrogen uptake kinetics [4]: the analysis revealed that the surface oxides hinder the H_2 molecular dissociation but do not act as an H diffusion barrier. Additional transition metal layers on top of the sample, in fact, restored completely the absorption kinetics.

In this paper we present an experimental study on the deuterium effusion from amorphous FeTi thin film based on thermal desorption spectroscopy (TDS) analysis. The aim of this study was to analyse the role of the surface oxide layers on the deuterium desorption kinetics and, in particular, to evidence if this oxide layer controls the D_2 desorption by limiting the surface processes.

2. Experimental procedures

Amorphous FeTi thin films (a-FeTi) were deposited by r.f. magnetron sputtering on (100) oriented Si wafers in a HV system with background pressure in the low 10^{-5} Pa range and provided by multiple target carousel. Thin film samples were grown at 150 W r.f. target power by using FeTi targets with nominal purity of 99.95 at.% and Ar at 0.5 Pa pressure as working gas. Some of the FeTi thin film samples were coated by a thin Pd capping layer without interrupting the vacuum conditions. The atomic composi-

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tion of the FeTi samples was evaluated by comparing energy dispersive spectroscopy (EDS) spectra with the spectrum of fragments taken from the target material: results indicated atomic composition ratio Fe:Ti=1.0 with concentration of oxygen and carbon lower than a few at.%. Deuterium uptake was carried out by exposing the samples at 573 K temperature to deuterium gas at 10^6 Pa pressure: the phase diagram of the FeTi–D system does not indicate the formation of any stable hydride phase in these thermodynamical conditions [5].

TDS analysis were performed in an UHV chamber equipped with a quadrupole mass spectrometer (QMS) [6]: experiments were carried out by heating the sample with a linear temperature ramp (0.5 K/s) and measuring the QMS D_2^+ mass signal ($m/e=4$) which is directly proportional to the deuterium desorption flux at a constant pumping speed of the vacuum apparatus. Experimental errors in the desorption flux were estimated from the mean value of the fluctuations in the $m/e=4$ background signal.

3. Experimental results

In Fig. 1a we present the XRD spectrum of the as-deposited sample (Cu Kα line): no signal pertinent to metallic Fe (α-Fe), metallic Ti (α-Ti) or Fe–Ti phases is observed thus proving that the deposited layers grow with high level of structural disorder. Similar XRD spectra were also obtained analysing FeTi samples annealed at 573 K in UHV conditions and FeTi samples annealed at 573 K in 10^6 Pa D_2 atmosphere. The formation of the FeTi intermetallic compounds with the CsCl structure in the present thin film samples only occurs after thermal annealing at temperatures greater than 750 K, as indicated by the XRD spectrum in Fig. 1b. This spectrum also indicates that no formation of any Si–Fe or Si–Ti compound occurs showing that atomic interdiffusion between substrate and coating is negligible. The conversion electron Mössbauer spectroscopy (CEMS) of the samples provide information on the local environment of Fe atoms: spectra were recorded at room temperature using a conventional flowing-gas proportional counter and a source of ^{57}Co of about 10 mCi activity in a Rh matrix. The spectrum of the as-deposited sample (see Fig. 2) can be fitted by an unresolved broad doublet with isomer shift (IS) of −0.23 mm/s and quadrupole splitting (QS) of 0.31 mm/s. These parameters are not corresponding neither to the h-Fe_2Ti Laves-phase (a doublet with IS=−0.29 and QS=0.40 mm/s [7]), nor to the FeTi phase (a singlet with IS=−0.15 mm/s [8]). This result confirms the XRD indication of a high level of structural disorder in the as deposited FeTi film. The CEMS spectrum of the sample annealed at 573 K in D_2 atmosphere shows again structural disorder but also a new component, a broad sextet, indicating α-Fe segregation (see Fig. 2). Because CEMS probes the surface region of the sample (50–100 nm), this spectrum suggests the formation of cluster-like Fe precipitates with size lower than a few nm (because they are not revealed by XRD spectra) in the near surface region of the a-FeTi film. This process is related to the reducing effect of the D_2 gas: the CEMS spectrum of an a-FeTi sample annealed at 573 K in UHV (see Fig. 2) does not present this α-Fe sextet and can be fitted by the doublet as for the as deposited sample without relevant changes in the IS and QS parameters.

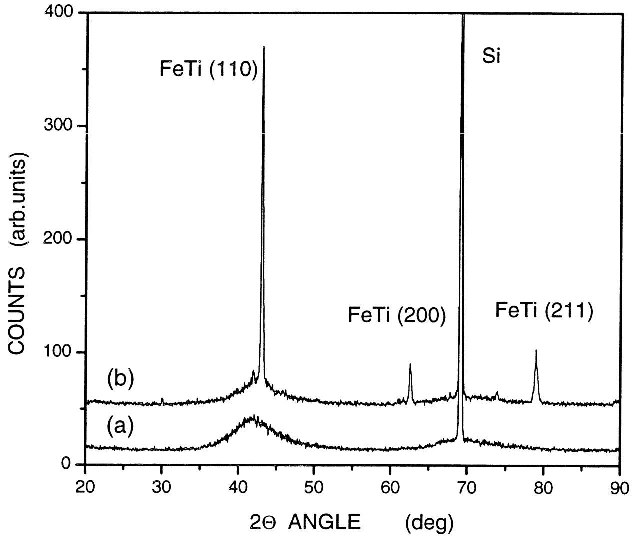

Fig. 1. (a) XRD spectrum of the as deposited a-FeTi thin film on (100) oriented Si substrate, (b) XRD spectrum of the FeTi thin film after thermal annealing at 800 K in UHV conditions for 4 h.

The TDS spectrum of an ~300-nm thick sample annealed in deuterium atmosphere is presented in Fig. 3: experimental data are presented as open symbols together with the experimental error, the solid line is the result of a numerical fit by Eq. (1) (see below). The spectrum presents a strong desorption peak at ~700 K with a shoulder in the low temperature side which disappears when the sample is submitted to further thermal treatments in D_2 atmosphere. By comparing the present TDS spectrum with that pertinent to a D-implanted sample with established fluence [9], we estimate a deuterium concentration in the a-FeTi sample of several at.%.

4. Discussion

When films containing deuterium are submitted to a temperature ramp, deuterium effusion occurs which can be simply analysed in terms of three rate limiting steps: detrapping of deuterium from the site where it is contained, diffusion through the host lattice and desorption from the surface. No structural change occurs during the effusion process because the a-FeTi sample does not contain hydride phase nor crystallizes during the TDS run (the TDS run is carried out at fast heating and the peak occurs at temperatures lower than ~750 K). An upper value for

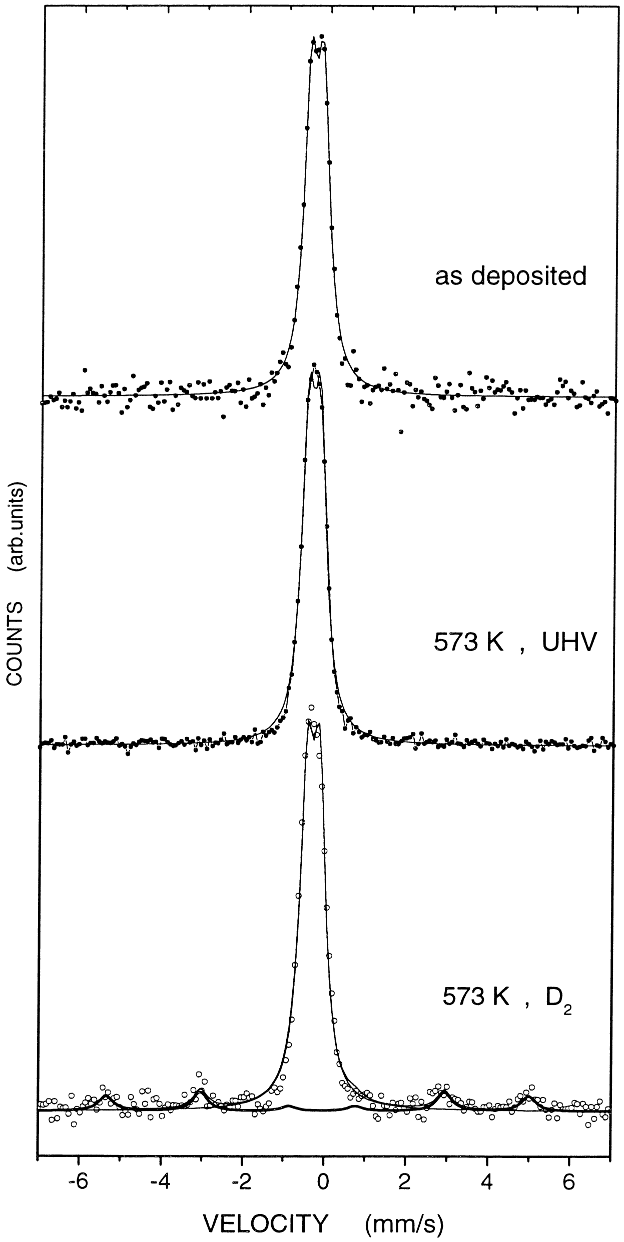

Fig. 2. CEM spectra of a-FeTi films as deposited, after treatment in vacuum and deuterium atmosphere. Open symbols, experimental data; thin continuous line, best fit; thick continuous line, metallic Fe component.

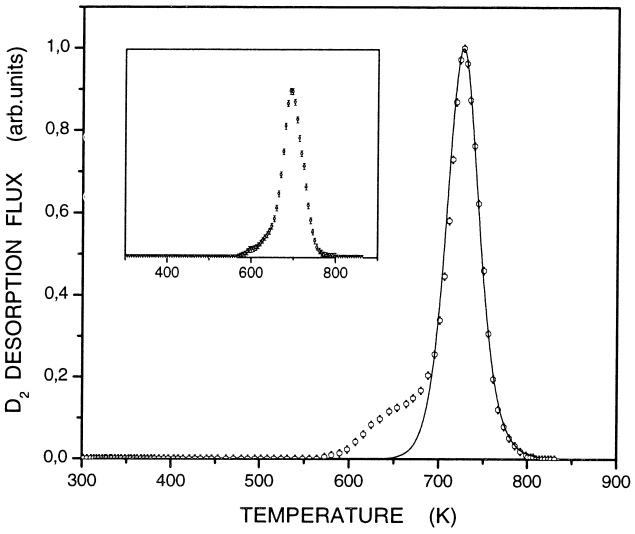

Fig. 3. TDS spectrum of a 300-nm thick a-FeTi thin film after thermal annealing in 10^6 Pa D_2 atmosphere at 573 K temperature. Solid symbols, experimental data; solid line, numerical fit obtained by using Eq. (1). In the inset we show the TDS spectrum of a 150-nm thick a-FeTi thin film.

the time of diffusion τ_{diff} can be evaluated by the relation $\tau_{\text{diff}} = l^2/D$, where $l = 300$ nm is the sample thickness and D the deuterium diffusion constant in FeTi. D is in the order of 10^{-9} cm^2/s [10] and τ_{diff} is 5–10 s approximately. This value is much lower than the present time for desorption $\tau_{\text{des}} \sim 10^2$ s, as estimated by the relation $\tau_{\text{des}} = \Delta T_{\text{P}}/r$, where $\Delta T_{\text{P}} \sim 200$ K is the peak width in the effusion signal and $r = 0.5$ K/s is the heating rate: we thus exclude the diffusion process as a rate-limiting step. This indication can be easily confirmed experimentally by comparing the TDS spectrum in Fig. 3 with the spectrum pertinent to a sample having lower thickness: no relevant shift in the peak position is observed with a 150-nm thick sample (see the inset of Fig. 3).

We have thus analysed the desorption data by using the reaction rate theory [11]: this theory assumes that deuterium atoms have to overcome an energy barrier ΔG in order to be evolved and that the frequency at which the barrier is confronted can be approximated by the factor $k_{\text{B}}T/h$, where k_{B} and h are the Boltzmann and Planck constants and T the absolute temperature. The effusion rate is evaluated by:

$$R_{\text{P}} = \frac{\mathrm{d}(c/c_{\text{p}})}{\mathrm{d}t} = \left(\frac{k_{\text{B}}T}{h}\right)\left(1 - \frac{c}{c_{\text{p}}}\right)^n \exp\left(-\frac{\Delta H - T\Delta S}{k_{\text{B}}T}\right) \tag{1}$$

where c_{p} and c are the original and evolved deuterium concentrations, n is the order of the reaction and $\Delta G = \Delta H - T\Delta S$ is the energy barrier. A good fit of the experimental data (see the continuous line in Fig. 3) can be obtained by assuming desorption as a second-order process ($n = 2$) with $\Delta H = 3.50 \pm 0.02$ eV and $\Delta S = (2.0 \pm 0.1) \times 10^{-3}$ eV/K. The evaluated value of the entropy variation ΔS is reasonable being similar to the entropy loss of hydrogen gas ($S = 130$ J/K mol H_2 at room temperature) upon absorption by solids [12]. As observed, for example, in the formation of Pd hydrides [13], excess entropy terms such as $\Delta S_{\text{H}}^{\text{vib}}$ representing the vibrational entropy of the absorbed hydrogen atoms, $\Delta S_{\text{host}}^{\text{vib}}$ reflecting the modifications in the vibrational spectrum of the metal matrix and ΔS^{el} which is due to the differences in the electronic heat capacity between the hydrogen-containing and the hydrogen-free compounds, are relatively small compared with the ΔS term relative to the entropy loss of the gas.

Being the peak temperature $T_P = 710 \pm 2$ K, an average value of 2.10 ± 0.05 eV can be estimated for ΔG.

Second-order desorption processes are often observed in desorption of light atoms, forming diatomic molecules, from solution in metals and are generally interpreted by assuming the recombinative desorption at the metal surface as the rate limiting process. The activation energy value measured in the present a-FeTi samples is larger than the values measured for the deuterium recombinative desorption in iron and titanium: depending on the Fe surface orientation, Boszo et al. measured values ranging from 0.9 to 1.1 eV [14], while in Ti we measured 1.52 ± 0.02 eV [15]. From the obtained ΔG value we can try to estimate the bond strength between D atoms and near-surface site where they are located. Assuming as negligible the energy barrier for physical adsorption, the value of the activation energy for desorption, ΔG, can be related to the strength of the surface FeTi–D bond through the relation $2E_{\mathrm{FeTi-D}} = \Delta G + E_{\mathrm{D-D}}$ [16], where $E_{\mathrm{D-D}} = 4.45$ eV is the binding energy of D_2 molecules. The value of 2.10 ± 0.05 eV indicates a binding energy $E_{\mathrm{FeTi-D}}$, of 3.28 ± 0.03 eV. The evaluated value indicates strong bonding of D atoms with surface sites probably on the surface oxides of the a-FeTi thin film. Oxide surfaces are known to be inert towards hydrogen molecules in gas phase, but atomic H interacts with the surface of stoichiometric oxides and the adsorption energies are quite strong when the interaction occurs with surface defects. H atoms interaction with O-vacancy defects at the TiO_2(110) surface, for example, results in bonding with the partially coordinated cations and produce Ti_4–H hydride bond [17]. H_2 absorption was observed in Ar ion bombarded TiO_2 surfaces and interpreted in terms of O–H bond formation by dissociation of the H_2 molecule [18]. The evaluated value of the $E_{\mathrm{FeTi-D}}$ energy is quite large and indicates that the FeTi–D surface interaction has a chemical character, probably by the formation of bonding with O surface atoms (the O–H bond energy is 4.5 eV [19]).

To verify that the observed deuterium desorption kinetics can be attributed to the surface processes active in the oxide layers of the a-FeTi thin films, we prepared two a-FeTi samples coated by a ~20-nm thick Pd capping layer [20]. In the first sample the Pd capping layer was deposited on the a-FeTi thin film surface without interrupting the vacuum conditions in the deposition chamber and the sample was then deuterated by thermal annealing at 573 K in 10^6 Pa D_2 gas pressure. This sample was produced to analyse the deuterium desorption kinetics from the oxide free a-FeTi. The TDS spectrum pertinent to this sample is presented in Fig. 4: it can be observed that the desorption peak at ~710 K completely disappears, and that deuterium is desorbed at temperatures lower than 500 K. To verify that the desorption kinetics of Fig. 3 is not controlled by the action of the oxide layer as diffusion barrier, we prepared a second sample by depositing the Pd capping layer on an a-FeTi film exposed to ambient conditions for a long time (1 month): deuteration was also carried out by exposing the Pd/a-FeTi sample to thermal annealing at 573 K in 10^6 Pa D_2 gas pressure. The TDS spectrum of this sample completely resembles the spectrum of Fig. 4 and confirms that the surface oxide layer limits the deuterium desorption kinetics by controlling the surface recombination of D atoms.

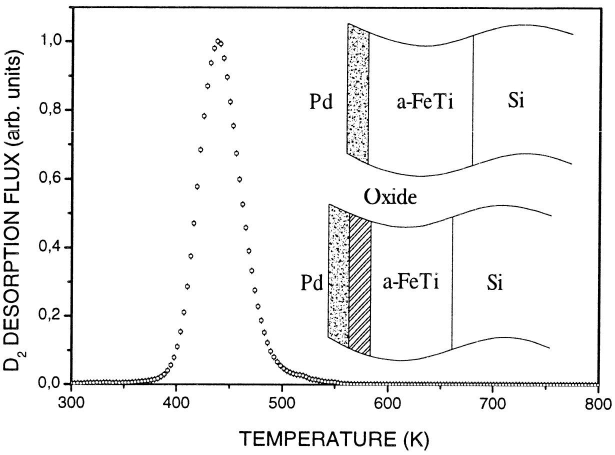

Fig. 4. TDS spectrum of a 300-nm thick a-FeTi thin film coated with a Pd capping layer.

The D_2 desorption temperature observed in the present Pd-coated FeTi samples is something higher than the hydrogen absorption–desorption temperature of FeTi powders with Pd catalyst [21]: we attribute this behaviour to the microstructure of our a-FeTi thin film samples different from that of nanostructured ball-milled samples.

In conclusion we have deduced from TDS analysis that the rate limiting process in the deuterium effusion from a-FeTi thin films is the recombinative desorption of deuterium atoms on the surface oxide layers. Desorption is an activated process with activation energy of 2.10 ± 0.05 eV which suggests chemical bonding of D atoms with O atoms at the sample surface.

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