Mg–Ti–H thin films for smart solar collectors

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Mg–Ti–H thin films are found to have very attractive optical properties: they absorb 87% of the solar radiation in the hydrogenated state and only 32% in the metallic state. Furthermore, in the absorbing state Mg–Ti–H has a low emissivity; at 400 K only 10% of blackbody radiation is emitted. The transition between both optical states is fast, robust, and reversible. The sum of these properties highlights the applicability of such materials as switchable smart coatings in solar collectors. © 2006 American Institute of Physics. [DOI: 10.1063/1.2212287]

Many metal hydrides behave as switchable mirrors (i.e., their optical properties switch from reflective in the metallic state to transparent in the hydrogenated state). In addition, magnesium–rare-earth (Mg–RE) and magnesium–transition-metal (Mg–TM) switchable mirrors also exhibit an intermediate highly absorbing optical state on hydrogenation. The possibility to switch a film from a reflective state to an absorbing state suggests that such materials might be interesting for smart solar collectors, which absorb light in normal operation condition and switch to a reflective state to avoid overheating. Limiting the stagnation temperature of the solar collector makes it possible to use cheap materials such as plastics (generally not designed for high temperatures).

In this letter we show that MgTi1–y thin films prepared by dc magnetron co-sputtering of Mg and Ti at room temperature (on quartz and CaF 2 ) satisfy the following requirements for a smart solar coating: (i) high absorption in the solar regime (0.5 < hω < 4 eV), (ii) low emissivity in the thermal regime (hω < 0.5 eV), and (iii) reversibility. Three compositions are studied in detail: y = 0.70, y = 0.80, and y = 0.90. Typical deposition rates are 2 Å/s for Mg (150 W rf power), 0.1–1 Å/s for Ti (25–160 W dc power), and 1.3 Å/s for Pd (50 W dc power). All the films are covered with a Pd layer (10–50 nm) to promote dissociation of H 2 and to prevent oxidation of the underlying film.

Reflection (R) and transmission (T) spectra are measured simultaneously during hydrogenation (pressures up to 1 bar H 2 ) in a Perkin Elmer Lambda 900 diffraction grating spectrometer (0.495 < hω < 6.51 eV) and a Bruker IFS 66 Fourier transform infrared spectrometer (0.2 < hω < 1.1 eV). The R–T spectra are measured through the transparent substrate at near normal incidence of the incoming beam. Figures 1(a) and 1(b) show the reflection and transmission spectra measured for 200 nm Mg10Ti0.80H y films (y = 0.90, 0.80, and 0.70) in the as-prepared and hydrogenated states (1 bar H 2 at room temperature). In the metallic state [Fig. 1(a)] all the films have a relatively high and featureless reflection that decreases with increasing Ti content.

After hydrogen absorption, the reflection is low for all compositions, whereas significant transmission is observed only for the y = 0.90 sample. The combination of low reflection and low transmission in the hydrogenated state (y = 0.80 and 0.70 samples) gives rise to a highly absorbing state that extends over the entire visible range. For example, Mg0.80Ti0.20H y absorbs ~87% of the solar radiation in the hydrogenated state and only ~32% in the reflective state.

FIG. 1. (Color online) (a) Reflection spectra measured on 200 nm Mg10Ti0.80H y films with y = 0.90, 0.80, and 0.70 in the as-prepared (metallic) and hydrogenated states (1 bar H 2 at room temperature). (b) Transmission spectra measured on the same films in the hydrogenated state. In the metallic state the transmission is below the detection limit of the spectrometer.
The highly absorbing state described here is a final state and not an intermediate optical state as in Mg–Ni–H (Ref. 5) and is thus robust and easily tunable. The same behavior is observed when using electrochemical loading. Again the reflection and transmission vary continuously (R decreasing, T increasing) until the maximum concentration of hydrogen is reached. Thus, this material can be applied both in electrochromic and gasochromic applications.

Despite the limited solubility reported for Ti in bulk Mg, alloying of Mg and Ti is obtained by using physical vapor deposition,6 mechanical alloying,7 or e-beam deposition.8,9 We observe a similar crystalline Mg–Ti alloy phase (hexagonal structure) when co-sputtering Mg and Ti. In hydrogenated films, the formation of a MgH2-like rutile phase is observed for low Ti contents (y=0.90), whereas in Mg–Ti–H with y=0.80 and y=0.70, a fluorite-like Mg–Ti–H phase is formed, similar to that identified by Kyoi et al.10 in bulk samples. There are no indications that phase segregation takes place as is the case for Mg–rare-earth systems such as Mg–Gd, Mg–La, and Mg–Y.11,12 The influence of phase composition and structure on the optical properties will be published elsewhere.

The optical properties of Mg5–yTiy–y and Pd layers. The thickness of the Mg–Ti–H layer is varied between 30 and 250 nm. As shown in Fig. 1, the absorption-to-reflective transition and transmission vary continuously, the x-ray amorphous films prepared by dc magnetron co-sputtering were reported to switch from reflective to transparent similarly to other Mg–TM (TM=Co, Ni, Fe, Mn), with Ti acting primarily as a catalyst for MgH2 formation.13 In comparison with the films studied here, their hydrogenated films do have similar low and featureless reflection, but also rather high transmission. Probably, due to the small thickness of their films (40–50 nm), the difference in the optical properties of the various hydrides does not show up.

For solar collector applications, it is desirable to have coatings that absorb as much solar radiation as possible, while emitting as little as possible in the thermal range. A set of 15 cycles measured for the first two cycles measured on 65 nm Mg–Ti –H/40 nm Pd (y=0.80) film in the as-prepared and hydrogenated states (1 bar H2 at room temperature). (c) Spectrum of the solar radiation at atmospheric mass (AM) of 1.5 shown together with the blackbody radiation at 400 K. Both are in arbitrary units.

For solar collector applications, the absorption-to-reflective speed, though it decreases slightly with increasing layer thickness, the absorption-to-reflective transition is thus very fast and rather independent of composition. An increase in Ti content has a beneficial effect on the absorbing-to-reflective speed, though it decreases slightly the optical contrast. A set of 15 cycles measured for the thermal range. The thermal emissivity of the system is calculated by extrapolating the absorption to zero energies and convoluting the data with the blackbody radiation at 400 K [spectrum shown in Fig. 2(c) together with the spectrum of the solar radiation at atmospheric mass (AM) of 1.5]. The result, a thermal emissivity of 0.10, is quite promising and, indeed, much lower than that of a thick film (~0.50).

A key issue for switchable coatings is the reversibility. This is tested by measuring reflection (through the transparent substrate) during gas cycling: hydrogenation with 5% H2 in Ar (250 ml/m flow) and dehydrogenation with 20% O2 in Ar (250 ml/m flow). Here we focus on the highly absorbing compositions (y=0.80 and y=0.70) that also show better switching properties as compared to the y=0.90 sample. In Fig. 3(a) we compare the reflection (hω=1.95 eV) for the first two cycles measured on 65 nm Mg–Ti1–y/H40 nm Pd films (y=0.70 and y=0.80). The reflective-to-absorbing transition is very fast and rather independent of composition. An increase in Ti content has a beneficial effect on the absorbing-to-reflective speed, though it decreases slightly the optical contrast. A set of 15 cycles measured for the
are comparable to that of advanced solar coatings such as 10% of blackbody radiation is emitted. These characteristics sorbing state Mg–Ti–H has a low emissivity; at 400 K only reducing the stagnation temperature. Furthermore, in the ab-
lication state, improving thus the solar absorption efficiency and diation in the hydrogenated state and only 32% in the metal-
ocoptimal configuration, the films absorb 87% of the solar ra-
have very attractive switchable optical properties that can be
is done with 5% H2 in Ar flow and unloading with 20% O2 in Ar flow.

FIG. 3. (Color online) (a) Reflection at hω=1.95 eV measured on 65 nm Mg,Ti1−yH films with y=0.70 and y=0.80; the first two cycles are shown. Hydrogen is introduced in the system at t=0, 730, and 1470 s; the start of the dehydrogenation period is indicated by the two arrows; loading is done with 5% H2 in Ar flow and unloading with 20% O2 in Ar flow. (b) Same measurements as in (a) but for more cycles.
y=0.70 sample is shown in Fig. 3(b). This result illustrates both the stability and reversibility of the system: the switching time from the reflective to the absorbing state is only a few seconds and stays rather constant similar to the optical contrast. Switching back to the reflective state is, however, slower and increases slightly with cycling. This effect could be related to poisoning of the Pd cap layer and/or intermix-
ing at the interface. Appropriate coatings and/or buffer layers can improve these performances.

Summarizing, we have shown that Mg,Ti1−y thin films have very attractive switchable optical properties that can be tuned by varying the composition and film thickness. In the optimal configuration, the films absorb 87% of the solar rad-
iation in the hydrogenated state and only 32% in the metal-
lic state, improving thus the solar absorption efficiency and reducing the stagnation temperature. Furthermore, in the ab-
sorbing state Mg–Ti–H has a low emissivity; at 400 K only 10% of blackbody radiation is emitted. These characteristics are comparable to that of advanced solar coatings such as ceramic-metal composite materials.16 Mg–Ti–H, however, has the great advantage of being switchable. The combina-
tion of these properties highlights the applicability of Mg–Ti–H thin films as switchable smart coatings for solar collector applications. Moreover, the fast switching together with the high optical contrast between the reflective and the absorbing states make Mg–Ti–H films also interesting for hy-
drogen sensor applications. The solar collector and sensor applications of Mg–Ti–H thin films described in this letter combined with the very large reversible hydrogen storage capacity of Mg–Ti–H thin film battery electrodes reported earlier by Notten and co-workers8,9 make this metal-hydride system truly remarkable.

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15Handbook of Optical Constants of Solids, edited by E. D. Palik, (Aca-