Journal of Alloys and Compounds 498 (2010) 26–29

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Heat pretreatment-induced activation of gadolinium surfaces towards the initial precipitation of hydrides

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ARTICLE INFO

Article history:
Received 4 January 2010
Received in revised form 1 March 2010
Accepted 6 March 2010
Available online 12 March 2010

Keywords:
Gadolinium
Hydride
Activation
Desorption

ABSTRACT

A vacuum heat pretreatment is applied, in order to enhance the reactivity of hydride-forming metals towards hydrogen reaction. For gadolinium, as for other rare-earth metals and some actinides, pretreatment temperatures of about 470 K are sufficient to induce such activation. The different factors that may be involved in that activation mechanism are identified and analyzed for gadolinium and their role is evaluated. It is concluded that the most prominent effect is desorption of surface hydroxyl groups, which impede the dissociative chemisorptions of hydrogen.

1. Introduction

It has been known for a long time that in order to enhance the initiation of hydriding reactions of hydride-forming metals, and shorten the induction periods that precede the corresponding hydrogen–metal reaction, vacuum heat pretreatment is necessary. Two types of such pretreatments were classified [1,2], one type relates to high-temperature treatments (i.e. at temperatures exceeding about 800 K) effective for a certain group of metals (e.g. Ti [3], Hf [4]), while other type relates to lower temperatures treatments (i.e. at about 440–500 K) effective for a different group of metals (e.g. the rare-earths or actinides [1,2]). It has been realized that the initial interaction of the H_2 gas phase with the reacting solid is actually (in "real life" metallic systems) with the surface oxidation overlayers that usually coat the metal surfaces. Hence, the observed induction periods that precede the hydriding reaction should be associated with the "passivation barriers" that these overlayers impose towards the penetration of hydrogen into the metals beneath [1,2]. The effects of the above mentioned heat pretreatments thus should arise from some changes induced by the corresponding heat pretreatments in the structure or composition of those oxidation overlayers. For the former high-temperature treatments, it has been suggested [1,2,5] that the main mechanism that induces the "activation" process involves redistribution of the surface oxide layer concurrent with surface segregation of the metallic component. This metallic component diffuses from the interface between the oxidation layer and the metal towards the outer surface, providing H_2 dissociative chemisorption sites and H diffusion paths that enhance the initials hydrogen penetration into the metal. For the lower temperature pretreatment, however, such metallic segregation is less effective and the induced activation may be related to other changes taking place within that temperature range. One possible factor that has been proposed [1,2] was the desorption of some functional groups present on the surface of the oxidation overlayer, especially hydroxyl groups that are known to desorbs within the relevant temperature range [6].

Even though the above suggested mechanism seems reasonable, it should be realized that besides hydroxyls desorption, some other changes may take place during the lower temperature heat treatments, and their role in the activation process should thus also be evaluated.

In the following discussion, three additional changes induced by heat pretreatments are presented and analyzed. These changes are:

(i) Desorption of other functional (carbon-containing) groups.
(ii) Release of surface stress induced by the mechanical polishing of the samples.
(iii) Diffusion of surface oxide into the bulk, resulting in oxygen deficiency at the near-surface region. This process, although less effective at lower temperatures, still cannot be ignored and must be analyzed quantitatively.

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doi:10.1016/j.jallcom.2010.03.080

Table 1
Different exposures of activated gadolinium samples (deactivation routes) and their possible contribution to deactivation. RH—relative humidity.

Gas exposure after activation (deactivation route)	Possible effects
(1) Humid air (30-40% RH)	• Re-oxidation (i.e. restoring oxygen deficiency lost by diffusion). • Re-hydroxylation. • Re-adsorption of desorbed carbon-containing gases.
(2) Moist oxygen (100% RH)	• Re-oxidation. • Re-hydroxylation.
(3) Dry oxygen	• Re-oxidation.
(4) Water vapor	• Re-oxidation. • Re-hydroxylation. • Hydride formation (see text).

The relative contributions of the above changes to the activation process were compared to that of the hydroxyls desorption.

This comparison was made by following the effects of the above activation-related parameters on the extent of the initial precipitation of gadolinium hydride under certain reference exposure conditions [7].

2. Experimental procedures

2.1. Polishing induced micro-strain analysis

Gadolinium samples, 99.9% pure, were polished to different smoothness levels (400 mesh, 1 μm) in order to form strained surface layers with different thicknesses. The extent of micro-strain in these layers was determined before and after thermal activation (preformed under the conditions specified in Section 2.2) by X-ray diffraction (XRD) line widths analysis.

2.2. The activation procedure and the reference hydriding reactivity test

The activation treatment applied in the present study included:

(i) Evacuating the sample at room temperature down to a back-pressure of about 10^{-4} Pa.
(ii) Heating the sample under vacuum to 470 K.
(iii) Keeping the sample temperature at 470 K for 1 h.
(iv) Cooling down to the ambient temperature.

The reactivity of either activated or deactivated (see Section 2.4) samples was determined by reference hydriding test which has been performed by exposing the sample to 600 Pa H_2 at 370 K for 480 s.

Under these reaction conditions the extent of hydride formation was determined in a semi-quantitative way by both AFM profile and XRD analyses [7] (and compared to the usual case of the activated samples).

2.3. Desorption of functional groups and oxide diffusion

The effect of the vacuum heat pretreatment on desorption of surface functional groups and oxide diffusion into the bulk was checked by applying two groups of techniques:

(i) Surface analysis measurements, incorporating two complimentary methods: Direct recoils spectrometry (DRS) [8,9] and X-ray photoelectron spectroscopy (XPS). The former technique has a unique sensitivity to topmost light atoms, including hydrogen (thus probes very effectively hydrogen-containing functional groups such as hydroxyls) whereas the latter one probes the chemical nature of oxygen and carbon-containing functional groups, enabling the identification of oxidic and hydroxylic groups.The gadolinium samples were polished to 1 μm roughness, rinsed with distilled water and alcohol, then introduced into the ultra-high-vacuum (UHV) chamber (back-pressure of about 10^{-8} Pa) and heated to the activation temperature (∼470 K). In situ DRS and XPS measurement were preformed on the gadolinium surface before and after the above heat treatment.
(ii) Thermal desorption spectrometry (TDS) measurements were performed in an atmospheric pressure cell using a QMS detector. A detailed description of the experimental setup may be found elsewhere [6,10]. Here, we only mention the principle key features that enabled the performance of the present study. Gd box samples, 3 mm × 2 mm × 10 mm, were placed inside a silcosteel coated cell enclosed by a concentric cylindrical furnace. A 1.5 bar helium carrier gas, flowing at a rate of 40 cc/min, was used to carry the desorbed products toward the QMS analyzer chamber via a heated transfer line, a nozzle and a skimmer. Under these conditions, the resulted supersonic beam travels through the mass spectrometer ion source, free of any collisions with the walls. Temperature scans were made at a rate of 15°/min and the peak intensities of some pre selected masses (H_2-2; H_2O-18; O_2-32; N_2/CO-28; CO_2-44) were continuously monitored as a function of the temperature up to 670 K.

2.4. Working scheme utilized to distinguish between contributions of the different activation-related parameters

When activated gadolinium samples are exposed to hydrogen gas, even at the ambient temperature range and pressures as low as about 600 Pa, the initial precipitation of small hydride spots (of the size of about 0.5–1 μm) takes place very rapidly (within 1–2 s) [7]. These hydride spots grow both, laterally and in height, with exponentially decaying growth rates and reach a certain limiting size (still in the sub-micron range). This behavior was attributed to the fact that the hydrides, at this early formation stage, are located beneath an intact oxidation overlayer that coats the sample's surface. Hence the growth process of the hydrides is impeded by the stress field that accompanies their expansion [7]. However, the initial appearance of these hydride spots at a certain time after hydrogen exposure, and their number density at such given exposure conditions are definitely related to the penetration rate of H across the oxidation overlayers into the metal interface. Hence, defining some reference exposure conditions (specified in Section 2.2) and analyzing the relative amounts of precipitated hydride spots (at this early precipitation stage) by AFM observations and XRD analysis, for different activation pretreatment parameters, may indicate the relative contributions of these parameters to the activation process.

The underlying approach which was used in the present study was to identify first the main parameters that are changed by the activation treatment. Then, following an activation treatment applying some controlled exposures to given gases that may restore only some of the changes induced by the activation (e.g. restoring a given functional group desorbed during activation). The effect of this exposure on the reactivity of the sample (towards hydrogen under the reference reaction conditions) is then checked (i.e. checking the effect of the restored parameter on deactivation of the activated sample). From such a series of exposures (henceforth denoted as "deactivation routes") the different activation-related parameters can be evaluated.

As in Ref. [7], all samples were first polished to 1 μm roughness (which induces a strained surface layer of about 2–3 μm, see Section 3). The different activation–deactivation routes utilize to separate between the possible heat pretreatments effects, are summarized in Table 1 (a detailed description of the changes induced by activation is presented in Sections 3.1 and 3.2).

In this table, route 1 (i.e. exposure to humid air) checks if restoring all chemical-diffusion surface changes induced by the activation treatment (but not stress-relief) actually results in deactivation. Under these conditions oxygen, which has been diffused into the bulk during pretreatment is replenished together with hydroxyl and carbon-containing species.

Route 2 distinguishes between effects of hydroxylation + oxidation and that of other carbon-containing gases contained in air (e.g. CO, CO_2).

Actually, in order to compare the hydroxyl groups effects to those of oxide diffusion (i.e. oxygen deficiency at the surface) it seems more simple to check the effect of pure water vapor exposure (route 4) to that of dry oxygen exposure (route 3) instead of comparing moist oxygen to dry oxygen. However, it has been found that after pure water vapor exposure (followed by heating under vacuum to 370 K), hydride precipitation took place even before hydrogen exposure. This was due to the water reduction reaction by the gadolinium, taking place at the near-surface region.

$$3H_2O + Gd \rightarrow Gd(OH)_3 + 3H_{ad} \quad (1)$$

With H_{ad} adsorbed neutral H atoms which then react to form the GdH_2 precipitate:

$$Gd + 2H_{ad} \rightarrow GdH_2 \quad (2)$$

Hence, the presence of a mixture of $Gd(OH)_3$ and GdH_2 that is formed for pure water exposure screens the determination of hydride development during the next H_2 exposure test (even though it seems from XRD and AFM analyses that no further

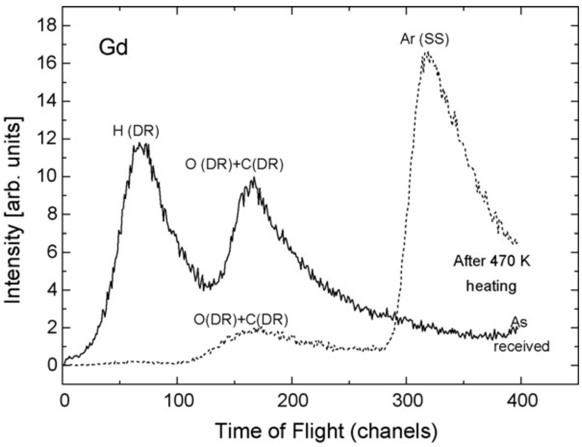

Fig. 1. DRS spectra of the gadolinium sample, as received and after heating to the corresponding "activation" pretreatment temperature (470 K).

significant development of hydrides occurred when the H_2O pre exposed surface was further exposed to H_2).

In order to avoid reactions (1) and (2), humid oxygen was then applied, which affects both, oxygen deficiency and hydroxyl restoration (but does not produce the hydride).

Then, in order to distinguish between the two factors (oxygen deficiency and dehydroxylation), dry oxygen exposure, which restores oxygen deficiency by not hydroxyls, was compared to the humid oxygen case.

3. Results and discussion

3.1. Heat-induced surface changes

Fig. 1 presents the DRS spectra of a gadolinium sample before and after heating (under UHV) it to the corresponding "activation" pretreatment temperature (~470 K). The strong attenuation of both, the hydrogen and the oxygen + carbon peaks is clearly evident. Fig. 2 presents the O 1s XPS peaks (before and after activation), indicating a heat-induced change from a hydroxylic type of oxygen into an oxidic type. Hence, the attenuation of the H(DR) peak in Fig. 1 and the shift in the O 1s XPS peak in Fig. 2 point to the desorption of hydroxyl groups during the applied treatment. The strong attenuation in the combined O + C DRS peak (Fig. 1) is partly due to the hydroxyls desorption, but is also due to the desorption of carbon-containing species. This is indicated in Fig. 3, where the C 1s XPS peak is displayed. It is seen that most of these carbon-containing groups are topmost adsorbed adventitious hydrocarbon species that desorb during the heat treatment.

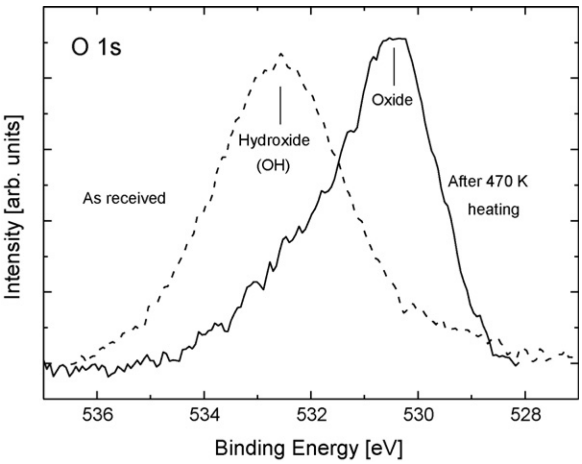

Fig. 2. O 1s XPS spectra – before (as received) and after heating, indicating a heat-induced change from a hydroxylic type of oxygen into an oxidic one.

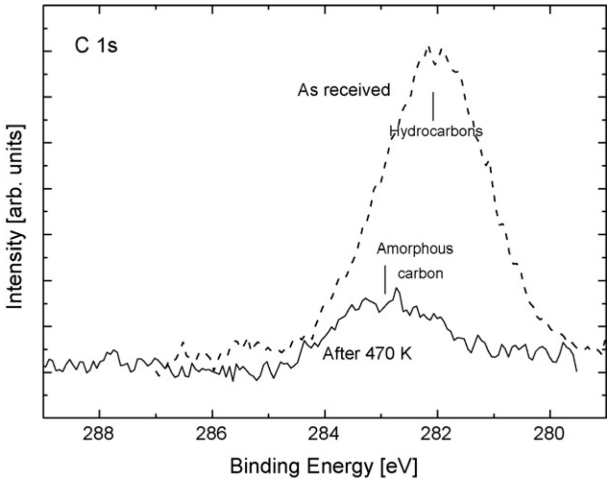

Fig. 3. C1s XPS spectra – before (as received) and after heating, indicating a heat-induced change from hydrocarbons to amorphous carbon.

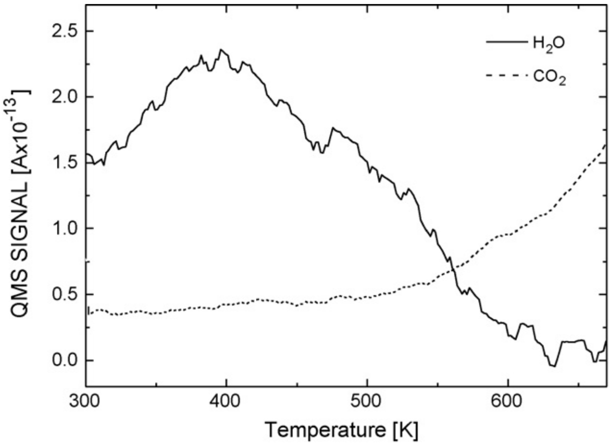

Fig. 4. TDS spectra of water and CO_2 emission, from the gadolinium sample, up to 670 K.

Fig. 4 presents TDS spectrum of water (m/e 18) and CO_2 (m/e 44) from gadolinium sample up to 670 K. Water desorption begins immediately after loading the sample to the reactor as can be seen from the high background water signal at room temperature. One broad peak with a maximum desorption rate at about 400 K is obtained. The desorption of water may originate either from weakly adsorbed water molecules on the oxidized surface or is due to hydroxide to oxide conversion. Since no trace of adsorbed water was detected in the XPS spectrum (Fig. 2, expected at ~534 eV), the second possibility is the probable one. At 500 K desorption of CO_2 starts and the desorption rate increases with increasing temperature. This desorption may originate from strongly chemisorbed ions of carboxylate ($CO_2{}^{-}$) or carbonate ($CO_3{}^{2-}$) on the oxidized surface. However, from XPS (Fig. 3) it seems that most of the carbon species are not associated with those species. We have also tried to check

Table 2
Strain induced by polishing and its thermal relief (as analyzed by XRD line width).

Treatment	Micro-strain (±5%)
Polishing to 400 mesh	2.0×10^{-3}
Polishing to 400 mesh + activation	1.0×10^{-3}
Polishing to 1 μm	1.5×10^{-3}
Polishing to 1 μm + activation	0.6×10^{-3}

Table 3
Results of the different deactivation routes summarized in Table 1 as observed after reacting the gas exposed sample to H_2 under reference hydriding test – see Section 2.2.

Deactivation route	Gas exposure	AFM observation	XRD relative intensities of hydride GdH_2 (0 0 2) peak to metal Gd (1 0 1) peak*
1	Moist air (~30% RH)	No hydrides	~0
2	Moist oxygen 100% RH)	No hydrides	~0
3	Dry oxygen	Hydride precipitation as in activated sample	0.09
4	Water vapor	Hydride precipitation due to water reaction (see text)	See text

* This ratio is about 0.07–0.09 for activated samples, and about 0 for non-activated ones.

the hydrogen desorption TDS peak. However the signal intensity was lower than our detection limit (~5–10 ng/s).

Preliminary Auger Electron Spectroscopy and DRS measurements show a certain effect of inward diffusion of oxygen during heating to 470 K which reduces the O/Gd ratio by about 40% in the oxide stoichiometry [11]. Hence, even at a relatively low temperature range (~470 K) non-negligible oxide diffusion takes place.

It is thus concluded that the most prominent chemical changes induced by heat activation treatment at 470 K are the desorption of water/hydroxyl groups and carbon-containing species and initial inward diffusion of the oxide overlayer.

3.2. *Heat-induced surface stress relaxation*

Table 2 presents the X-ray line width analysis of two polished samples (400 mesh and 1 μm polishing) before after heat treatment activation.

It is evident that the treatment under “activation” conditions relaxes the polishing induced micro-strain in the near-surface region. For the 1 μm polished sample a relaxation of about 60% is apparent.

3.3. *Restoring deactivation of activated samples by the different working routes*

Table 3 summarizes the effects of the various gas exposures on the deactivation of the activated samples.

It is concluded that the main factor that induces deactivation is the hydroxylation (which takes place during routes 1, 2). The effect of oxygen deficiency due to oxide diffusion (restored by route 3) dose not seem to contribute significantly at this activation temperature range. Also, stress relaxation does not seem to affect the activation–deactivation since the deactivation which has been obtained for the re-hydroxylated, stress-relieved samples, was similar to that of the stressed ones.

The above conclusion is consistent with that proposed previously [1,2], that attributed the activation process of uranium samples to dehydroxylation. It has been pointed out that hydroxylation of oxide catalysts may poison their activity towards hydrogenation reactions or hydrogen isotope exchange kinetics [12]. It is thus likely that hydroxyls present on oxide surfaces may impede the dissociative chemisorptions of H_2, and thus reduce the penetration rate of hydrogen through the oxide surface layers.

4. Conclusions

1. In order to enhance hydride formation on metallic surfaces, heat treatment under vacuum (henceforth denoted as “activation”) is applied. For Gd, the activation process incorporates heating at about 470 K under high vacuum for about 1 h.
2. During activation treatment of polished Gd samples, four heat-induced changes take place, at the near-surface region:
   (i) Stress relaxation (of the stress induced by polishing).
   (ii) Oxygen deficiency, caused by partial diffusion of surface oxide into the bulk.
   (iii) Desorption of carbon-containing adsorbed species.
   (iv) Desorption of chemisorbed hydroxylic groups.
3. The main factor that was identified to be involved in the activation–deactivation phenomena is the presence of hydroxyl groups on the surface of the oxidation layers that cover the samples. These hydroxyls seem to impede the dissociative chemisorption of H_2, hence slowing down the penetration rate of H across the oxidation surface layer.

Acknowledgements

This work was partially supported by a grant from the Israel Council for Higher Education and Israel Atomic Energy Commission and a grant from the Ministry of National Infrastructure Division of R&D.

The authors wish to thank Mr. Yaron Alfi and Mr. Shlomo Levi for their technical support.

References

[1] J. Bloch, E. Swissa, M.H. Mintz, Z. Phys. Chem. NF 164 (1989) 1193.
[2] J. Bloch, M.H. Mintz, J. Less-Common Met. 166 (1990) 241.
[3] A. Efron, Y. Lifschitz, I. Lewkowicz, M.H. Mintz, J. Less-Common Met. 153 (1989) 23.
[4] Y. Levitin, J. Bloch, M.H. Mintz, J. Less-Common Met. 175 (1991) 219.
[5] E. Swissa, N. Shamir, M.H. Mintz, J. Bloch, J. Nucl. Mater. 173 (1990) 87.
[6] A. Danon, J.E. Koresh, M.H. Mintz, Langmuir 15 (1999) 5913.
[7] G. Benamar, D. Schweke, J. Bloch, T. Livneh, M.H. Mintz, J. Alloys Compd. 477 (2009) 188.
[8] M.H. Mintz, J.A. Schultz, J. Less-Common Met. 103 (1984) 349.
[9] J.W. Rabalais, CRC Crit. Rev. Solid State 14 (1988) 318.
[10] A. Danon, I. Avraham, J.E. Koresh, Rev. Sci. Instrum. 68 (1997) 4359.
[11] S. Cohen, unpublished results.
[12] F.P. Netzer, E. Bertel, Adsorption and Catalysis on Rare Earth Surfaces, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, North-Holland Publ. Co., Amsterdam, 1982, pp. 217–320.