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Effects of pre-dissolved hydrogen on the precipitation and growth kinetics of gadolinium hydride on polycrystalline gadolinium surfaces

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Abstract

The kinetics of precipitation of hydride growth centers (GCs) as well as the growth velocities of the individually growing precipitated hydride 'patches' on polycrystalline gadolinium surfaces have been the subject of some recent studies. Hot stage microscopy coupled with a CCD camera enabled the evaluation of the precipitation rate functions and growth velocities at various reaction conditions and pre-treatments of the reacting surfaces. One of these pre-treatments has been to dissolve hydrogen into the near-surface zone prior to the hydriding step, by pre-exposing the surface to low pressure hydrogen under conditions that no growth centers are yet formed. Such a treatment has a most significant deleterious effect on the kinetics of precipitation and growth of the subsequent hydriding step. These observations contradict the intuitive expectation of an opposite trend, i.e. enhanced hydriding kinetics due to the presence of the pre-dissolved hydrogen that is already available at the reacting zone. Possible mechanisms for such a hydrogen induced 'passivation' effect are proposed.

Keywords: Pre-dissolved hydrogen; Gadolinium hydride; Polycrystalline gadolinium surfaces

1. Introduction

Utilization of in-situ direct optical microscope observations (hot stage microscopy, HSM) of the initial development of hydrides on polycrystalline metallic surfaces exposed to hydrogen, revealed certain interesting features associated with these processes [1–8]. For non-brittle metals or alloys (including most of the binary metal–hydrogen systems and probably some intermetallics), the incipient stage of hydriding is characterized by the appearance of growing hydride 'spots' (or 'patches') on the metallic surface. These 'spots' (referred to as growth centers, GCs [8]) start to precipitate after a certain induction time, t_i, which is determined by the reaction conditions (P,T) and the characteristics of the reacting surface [8]. The rate of the precipitation process of the GCs is not constant but rather displays a time function with a maximum. The shape parameters of these rate functions (the width and the location of the maximum) depend on the reaction parameters (P,T and surface characteristics). Recently, a kinetic model has been proposed to account for these complex precipitation features and their temperature and pressure behavior [8]. The model yielded simple analytical forms for the precipitation rate functions, which fitted well the experimental data obtained for certain metal–hydrogen systems.

In addition to the rate of precipitation (or 'nucleation') of the hydride GCs, the growth kinetics of individually growing hydride 'patches' can also be measured by these in-situ HSM observations. In certain systems (e.g. Ce–H [5] or U–H [6]) average constant (i.e. time-independent) growth velocities were obtained under given reaction conditions (i.e. P,T). However, unlike the precipitation characteristics, these growth velocities were not sensitive to the variations in the surface properties of the reacting sample (e.g. to surface modifications by ion implantation [6,9]).

The detailed precipitation and growth kinetics of the hydride phase on polycrystalline gadolinium surfaces have been the subject of some recent studies [8,10,11]. In this system, a new phenomenon related to the growth velocities of the hydride 'patches' was observed [11]. It was found that, under given reaction conditions, the growth velocity is not necessarily constant (as obtained so far for other systems), but may fluctuate during certain time intervals

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between two different ranges, i.e. 'slow' and 'rapid'. Hence, by following the velocity of the hydride–metal interface of a specific 'patch' growing along a given direction on the surface, it is occasionally apparent that this velocity changes abruptly from a high value to a significantly lower value, or vice versa. The two extreme values of the velocity, the rapid one, $U_{\max}$, and the slow one, $U_{\min}$, may differ by as much as an order of magnitude [11].

In the present study, the effects of hydrogen pre-dissolution on the above-mentioned precipitation and growth processes of the hydride have been determined. In these experiments, the gadolinium samples were pre-exposed to hydrogen at a low pressure prior to the following higher-pressure exposure step, which led to the hydride precipitation. Hence, a certain H concentration profile already existed at the near-surface region of the samples when the reaction conditions were set. Intuitively, it was anticipated that such a H pre-dissolution procedure would facilitate the precipitation and growth processes since attainment of the limiting solubility limits required to initiate hydride precipitation [8] would seem to be easier and faster. Surprisingly, the converse effect was obtained, i.e. hydrogen pre-dissolution had a significant deleterious effect on both the precipitation and growth processes.

2. Experimental

Pure gadolinium (99.9%) samples were mechanically polished to ±1 μm roughness, cleaned with alcohol and placed in a high vacuum reaction chamber of a hot stage optical microscope (HSM) [5]. A grain size of the order of 30–50 μm and oxide thickness of about 100–300 Å typically characterized these samples. Continuous observations and recording of the polished face of the sample were performed during the following pre-treatments and reactions.

The samples were first outgassed under dynamic high vacuum (~10^{-5} mbar) at 300°C for 1 h, then cooled to 200°C and then each sample was exposed to low-pressure (10 mbar) hydrogen for various periods of time (ranging from 1 to 16 h). Under these low-pressure exposures, no precipitation of a hydride phase was observed within the resolution limits of the optical microscope (~1 μm).

It should be noted that the equilibrium dissociation pressure of GdH_2 at 200°C is about 10^{-12} mbar [12] which is well below the 10 mbar pressure applied in the system. Still, as discussed in previous articles [8], the precipitation of a hydride phase at the oxide–metal interface is accompanied by a significant compression field (due to the expansion of the hydride phase embedded in the surrounding matrix). Such compression fields may raise the chemical potential of the formed precipitates, leading to minimum reaction pressures much higher than those characteristic of the equilibrium dissociation pressures.

The low-pressure pre-exposure step thus mainly induced the dissolution of hydrogen into the near-surface region, producing a certain H concentration gradient, related to the exposure conditions (i.e. under the fixed pre-exposure temperature and pressure). This concentration profile depends on the exposure time, which, as stated above, ranged between 1 and 16 h.

At the end of the above pre-exposure stage the low-pressure hydrogen atmosphere was quickly raised to 1000 mbar, at the same temperature of 200°C. The time-dependent rate function of formation of the hydride GCs and the growth velocities of some selected hydride 'patches' (along different directions for a given 'patch') were established for the different pre-exposure periods. The data analysis procedure was the same as described previously for non-exposed samples [8,11].

3. Results

Fig. 1 presents a reference sequence of pictures related to the development of the hydride on the non-exposed samples [8,11], for the same reaction conditions (i.e. 1000 mbar, 200°C). Fig. 2 presents a comparison with the samples pre-exposed to low-pressure hydrogen for 1 h. Figs. 1 and 2 represent different time intervals between the frames even though both experiments were performed under the same temperature and hydrogen pressure. The hydride GC sizes in the figures are determined by both the exposure time and the surface velocity and thus cannot be compared by just a visual observation of the two figures.

A dramatic change in the rate of GC formation is evident from these observations. The pre-exposure step seems to significantly reduce the number, and rate of precipitation, of growing hydride patches on the gadolinium surface.

It should be noted that, for both cases (pre-exposed and non-exposed samples), the location of preferred precipitation sites is the same, i.e. at grain boundaries and edge dislocations [8]. The only difference is the number (or rate) of precipitates that grow on the sample surface, which is reduced by the pre-exposure step.

In addition to the effect of hydrogen pre-dissolution on the hydride precipitation rate, a significant effect was also observed concerning the induction periods which precede the initial precipitation of the first hydride nucleus [8]. These induction periods seem to increase with increasing pre-exposure time. Table 1 presents some quantitative values for these induction periods, and densities of hydride precipitates (at the times denoted in brackets), as a function of the pre-exposure duration.

It should be pointed out that, according to a recent kinetic model (which was justified for gadolinium and uranium hydrogenation experiments), the number density, $N(t)$, of GCs developed at time t is given by [8]

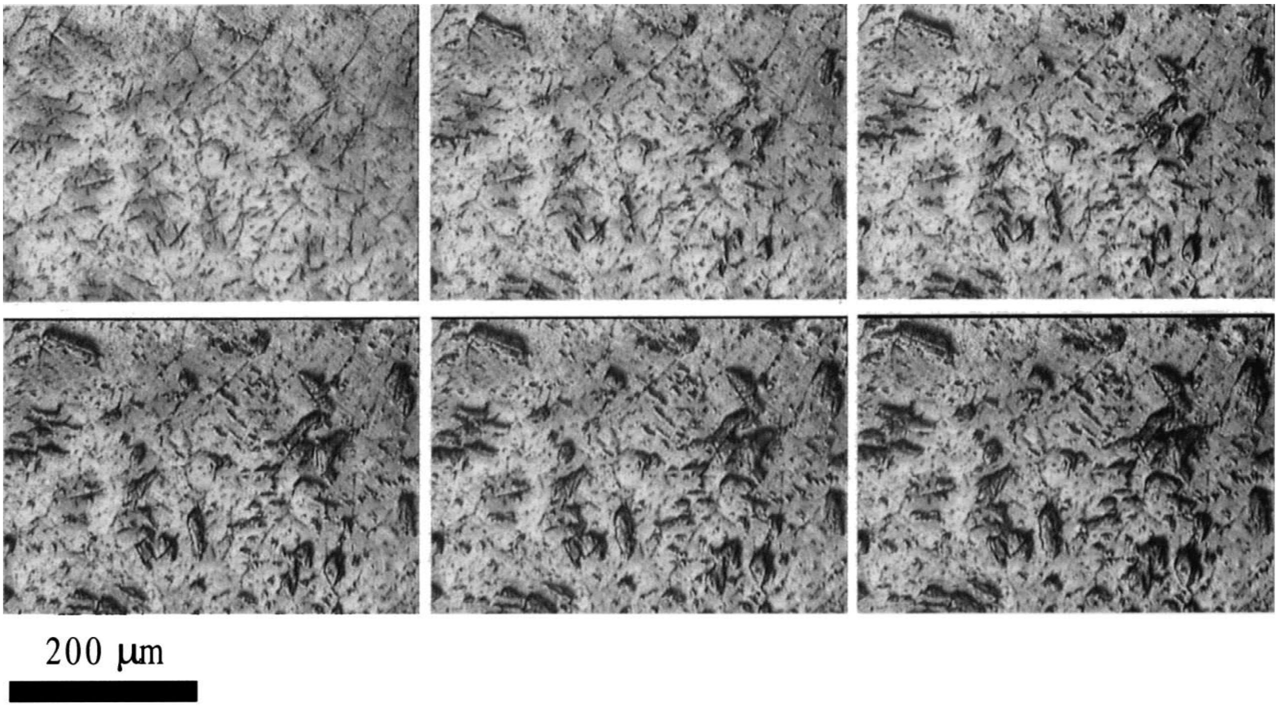

Fig. 1. Time evolution of hydride precipitates on a hydrogen-free polycrystalline gadolinium surface. The pictures series (starting from the left, ending bottom right) correspond to *t* = 0, 2, 3, 4, 5 and 6 s after hydrogen introduction into the reaction chamber. Hydriding was performed at 200°C under 1000 mbar H_2.

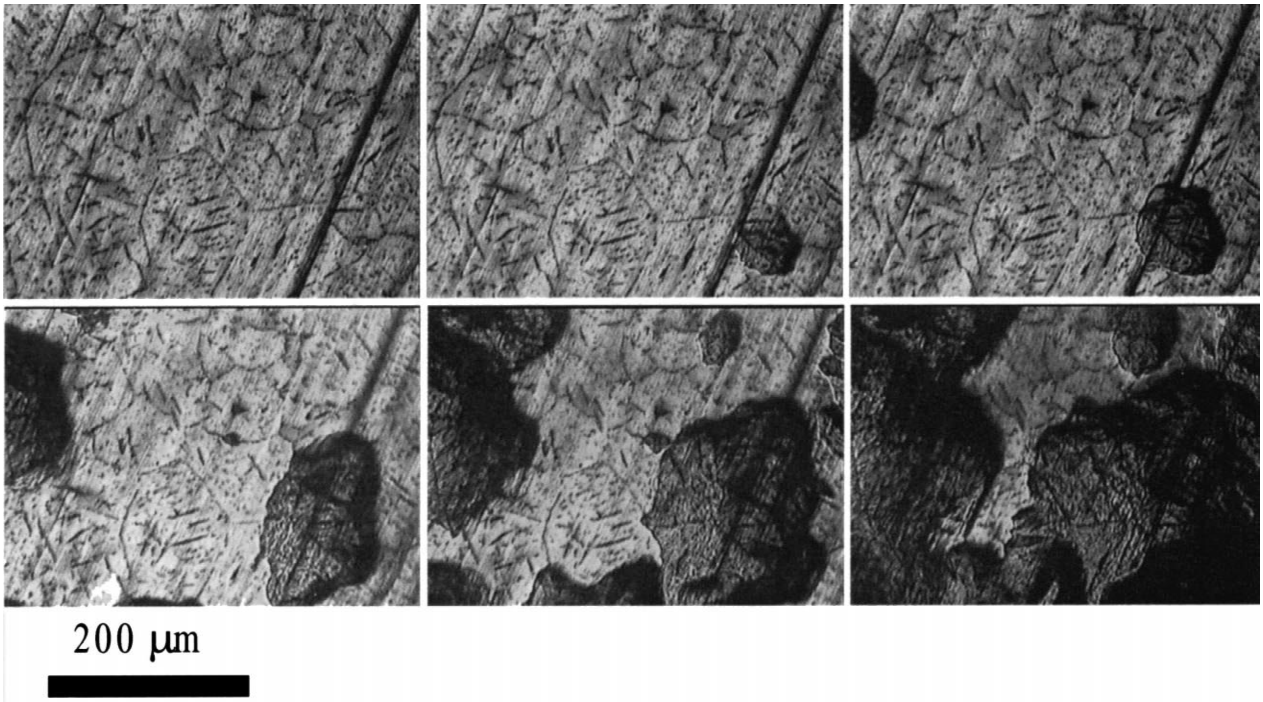

Fig. 2. Time evolution of the hydride phase on a polycrystalline gadolinium surface pre-exposed to low-pressure (10 mbar) hydrogen at 200°C for 1 h. The hydriding conditions were the same as in Fig. 1. The series of pictures correspond to *t* = 0, 20, 30, 40, 50 and 60 s after the introduction of 1000 mbar H_2 pressure.

Table 1
Influence of pre-exposure time on the nucleation induction time and nucleation density (given at time t, setting $t^{1/2}-t_i^{1/2}$ to a fixed value)

	Pre-exposure time (h)		
	0	1	16
Induction period, t_i (s)	1–2	~20	~1300
Density of GCs, $N(t)$	$3\cdot10^4$	$\sim2\cdot10^3$	$\sim10^2$
(cm^{-2}) [at time t (s)]	[12]	[50]	[1500]
($t^{1/2}-t_i^{1/2}$) ($\text{s}^{1/2}$)	2.24	2.59	2.67

$$N(t)=N_0\{1-\exp[-k(t^{1/2}-t_i^{1/2})^2]\},\quad t\geq t_i \tag{1}$$

where N_0 is the total number of available precipitation sites, k the (temperature-dependent) precipitation rate constant, and t_i the (temperature-dependent) induction time.

Hence, it is evident from Eq. (1) that, under given reaction conditions, increasing t_i should lead to a reduction in $N(t)$ over a comparable time scale. The question which may then be addressed is: does the pre-exposure step reduce $N(t)$ just by resulting in an increase in t_i, or does it also affect N_0 and k?

In order to resolve these possible effects, the number densities, $N(t)$, in Table 1 were chosen at corresponding times t to make ($t^{1/2}-t_i^{1/2}$) about the same for all pre-exposure durations. According to Eq. (1), under such time scales, $N(t)$ should be the same, if no changes in N_0 or k take place.

It is evident from Table 1 that $N(t)$ is reduced by the pre-dissolution step, much beyond its effect on t_i. Hence, in addition to an increase in the induction period, hydrogen pre-dissolution also affects either the type (and number) of available precipitation sites, N_0, or the precipitation rate constant, k.

Finally, the effect of H pre-dissolution on the growth velocities of the hydride precipitates is considered. As described in Ref. [11], when choosing a certain individually growing 'patch', a given growth direction along the surface and plotting the position of the hydride front advancing in this direction as a function of time, the front displacement versus time curve has the typical form illustrated in Fig. 3 (for a non-exposed sample). Hence, it is observed that sudden changes in the slopes (i.e. in the growth velocities) occasionally occur. For the non-exposed samples it has been reported [10] that, under given experimental conditions (T,P), the fluctuations in the growth velocities range between two extreme values, a maximum, $U_{\max}(T,P)$, and a minimum, $U_{\min}(T,P)$.

Such behavior has also been observed for H pre-dissolved samples. However, the corresponding growth ve-

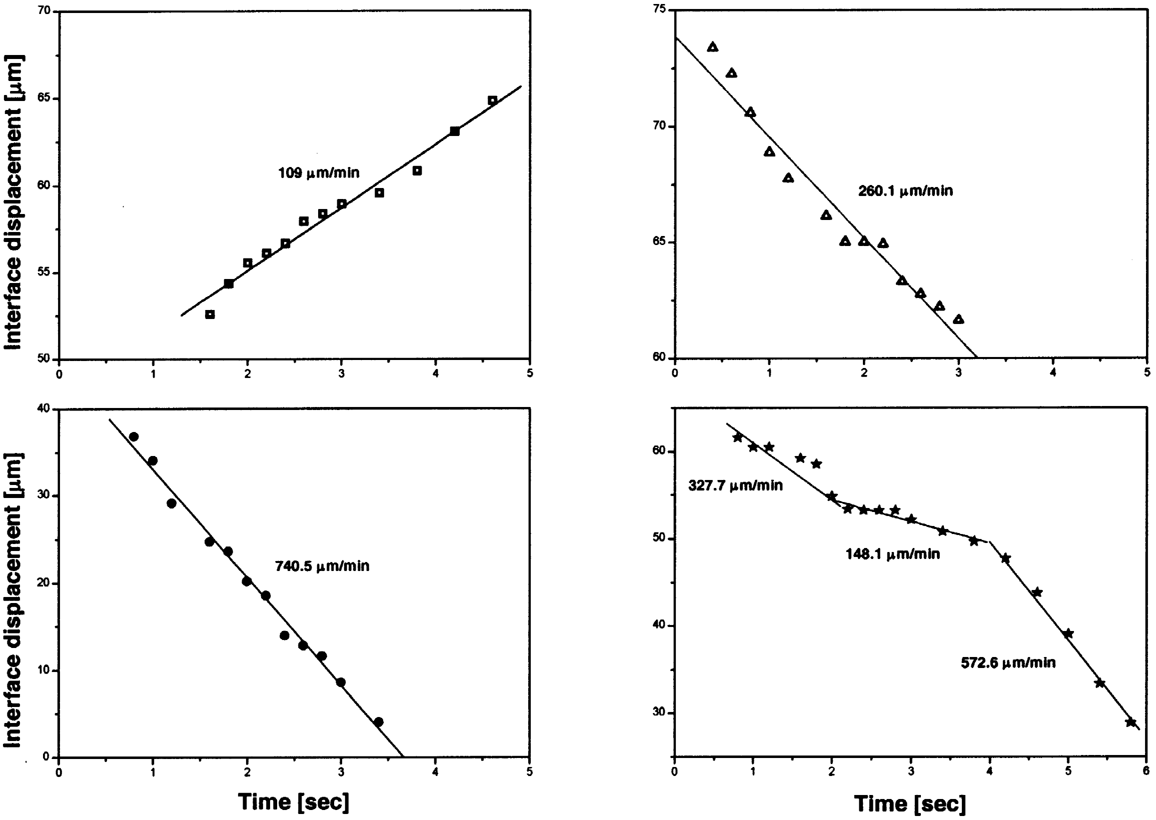

Fig. 3. Reaction front displacement position versus reaction time for the growth of hydride 'patches' on polycrystalline gadolinium (initially hydrogen-free). The different pictures represent either different growth directions for a given 'patch' or those of different 'patches'. Growth velocity fluctuations are occasionally observed.

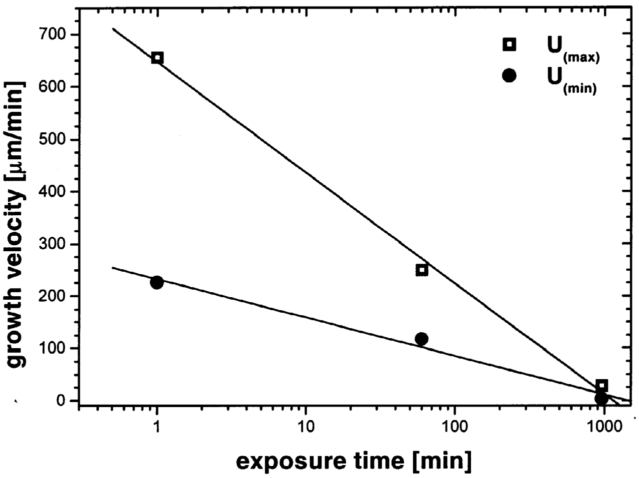

Fig. 4. High-velocity, U_{max}, and low-velocity, U_{min}, extreme values observed for growth of hydride precipitates on gadolinium (see Fig. 3) as a function of the exposure time to low-pressure (10 mbar) hydrogen. The hydriding reaction conditions are the same as in all previous figures (200°C, 1000 mbar H_2).

locities, and especially U_{max}, were reduced by the pre-dissolution process. Fig. 4 presents the values of the above two extreme growth velocities as a function of the time period of the pre-exposure step. It can be seen that the most significant reduction occurs for U_{max}, which finally leads to the convergence of the two different velocities into a single (low value) velocity for the higher pre-exposure periods.

4. Discussion

The whole set of results above indicates that when hydrogen is pre-dissolved in the near-surface zone it has a significant deleterious effect on the development of the hydride phase (under higher reaction pressures). The pre-existence of a H concentration profile impedes both the precipitation (nucleation) of the hydride, as well as its growth velocity. Such a trend contradicts the intuitive prediction of an acceleration of hydride development under these conditions. It is well known that in order to initiate a metal-to-hydride transformation, a limiting H concentration (the so-called solubility limit) should be exceeded. Hence, if a certain finite H concentration already exists at the near-surface zone, the attainment of these solubility limit concentrations should be faster, leading to an enhancement of the hydride nucleation and growth processes.

Several possible explanations may be proposed to account for the above surprising H pre-exposure effects. First, a possible hydrogen-induced annealing effect can be assumed. As stated in Section 2, the gadolinium samples went through a mechanical polishing treatment prior to their introduction into the reaction chamber. It is well known that mechanical polishing induces strain fields and concomitant defects in the near-surface region. Such a strained zone may react faster than an annealed, strain-relieved zone. If H dissolution affects the diffusion rates of the surrounding matrix atoms, e.g. by stress-enhanced mechanisms [13], this may result in hydrogen-assisted strain relaxation phenomena, which might account for the decelerated reactivity of the H pre-exposed surface. With respect to this possibility, it should be considered that an additional annealing step is applied to the samples during the outgassing treatment (300°C/1 h, see Section 2). Hence, this explanation is reasonable only if this step is not sufficiently effective in relieving the polishing-induced mechanical strain.

In order to verify this approach, X-ray diffraction (XRD) measurements of the following samples were made:

(a) a mechanically polished sample, prior to the heat outgassing treatment;
(b) a sample of (a) after outgassing at 300°C for 1 h;
(c) a sample of (b) after the low-pressure hydrogen exposure step (exposure time ~1 h).

The XRD lines of the polished gadolinium sample are indeed very wide, indicating the presence of stress fields at the near-surface zone. However, the outgassing heat treatment applied to the samples seems to be adequate in relieving most of the stresses, restoring the XRD line widths to their narrow ‘normal’ widths. The following hydrogen pre-exposure step does not result in any further changes in these line widths, indicating that there were no further stress relaxation or annealing effects due to H pre-dissolution. Hence, the above hypothesis relating the impediment of hydride phase development to H-induced annealing phenomena is not supported by XRD measurements.

A possible alternative explanation for these pre-exposure effects may arise from the volume expansion of the H-modified zone. However, within the experimental accuracy of XRD, no changes in the unit cell constants of the H-exposed samples were apparent. It thus seems that neither of the two mechanisms proposed above can be substantiated by XRD measurements, which might have inadequate sensitivity to such subtle changes.

Evidently, more detailed studies are still required in order to understand these complex precipitation and growth processes of hydride phases on metallic surfaces.

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