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The very initial stage of hydride formation on polycrystalline gadolinium

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ABSTRACT

The initial development of hydrides on hydrogen-exposed metallic surfaces displays a complex behavior with two possible surface-associated stages [M.H. Mintz, in: K.H.J Buschow, R.W. Cahn, M.C. Flemings, B. Ilschner, K.J. Kramer, S. Mahajan (Eds.), Encyclopedia of Materials: Science and Technology, Elsevier Sci. 2002, pp 1–9; Y. Ben-Eliyahu, M. Brill, M.H. Mintz, J. Chem. Phys. 111 (1999) 6053]: (i) Rapid formation of a dense pattern of small (sub-micrometric) hydride spots, which almost instantaneously attain their near final size and practically cease any further development (resulting in a type of “induction” or “incubation” period). (ii) Development of a few “growth centers” (GC’s) of hydride “patches”, which spread over the surface and lead to the massive hydriding stage.

In the present study, the features of the very initial stage (i.e., stage (i)) are characterized for the H_2/Gd (polycrystalline) system, using Hot Stage Microscopy (HSM), X-ray diffraction analysis and Atomic Force Microscopy (AFM) techniques.

The main characteristics are:

(1) Typical hydride nucleation patterns composed of dense overlapping “spots” aligned along certain orientations on given metallic grains.
(2) Very rapid initial development rates (within seconds), followed by an exponential decay of the precipitate growth rates.
(3) A strong dependence of reactivity on the orientation of the metallic grains, with some grains displaying a very high reactivity (i.e., formation of very dense nucleation patterns) and other grains displaying a long-term inertness.
(4) A time delay (“induction” period) between stage (i) and the flowing stage (ii) (i.e., GC’s formation), which predominantly depends on the hydriding pressure and temperature.

The above features and their related kinetics were studied as a function of hydrogen pressure (in the range 6×10^2 to 2×10^4 Pa) at 373 K.

Possible mechanisms controlling these reactions are discussed.

1. Introduction

The development of the hydride phase on hydrogen-exposed metallic surfaces of hydride-forming metals (or alloys) is a complex process involving multi-scale stages, each controlled by a certain rate determining mechanism [1–3].

The incipient stages of this process are often characterized by the appearance of hydride “spots” or “patches” on the surface (especially for the binary M–H systems).

In fact, two types (or “families”) of hydride precipitates were identified [1–3]: (i) a dense pattern of tiny (sub-micron) spots, which form immediately after hydrogen exposure, attain their final size (in the sub-micrometric range) and practically cease a noticeable further development and (ii) following stage (i), after a certain “induction time” development of some “growth centers” (GC’s) of hydride “patches” which spread over the surface, and lead to the so-called “massive” hydriding stage.

The kinetics of the latter stage were followed by in situ Hot Stage Microscopy (HSM) observations, and a quantitative kinetic theory was proposed to account for the time dependence and pressure–temperature behavior of this process [2]. However, the detailed characteristic and kinetic behavior of the very initial stage (i.e., stage (i)) are still not elaborated.

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It has been reported that pre-exposing gadolinium to low-pressure hydrogen (10^3 Pa, 573 K) for a few hours, had a significant deleterious effect on the precipitation kinetics of GC's when those pre-exposed samples were further hydrided under higher pressures (10^5 Pa). For these pre-exposed samples, the induction periods for the appearance of the first GC's were much longer and the densities of the precipitated GC's were significantly lower than the corresponding kinetic parameters of the ordinary (not pre-exposed) specimen. It was claimed that no hydride precipitation could be detected during the low-pressure exposures, and the effects of these treatments was attributed to dissolution of hydrogen in the near-surface region [4]. However, as described further in this article a tiny (sub-micrometric) hydride "family" does precipitate even for lower pressure exposures (in the range applied in reference [4]).

Hence, it is more likely that the appearance of such tiny hydride spots could actually not be detected by the lower magnification optical observations utilized in the above article [4].

It is the purpose of the present study to clarify the kinetics of the very initial hydride precipitation process, characterize its quantitative time behavior and propose a possible mechanism associated with this early development stage of the hydride. The model system chosen for this purpose was polycrystalline gadolinium, on which some kinetic data has been reported on the initial development stages of hydrides [2,4].

2. Experimental

Hydrogen exposure experiments were performed in a high-vacuum chamber (base pressure of about 10^{-4} Pa) of a Hot Stage Microscope (HSM), utilized in previous studies of the GC's kinetics (described in detail in references [5,6]).

Polycrystalline gadolinium samples were polished down to 1 μm roughness, glued to a specially designed holder and inserted into the HSM chamber. The Torr-Seal glue was checked to be compatible with the sample and not to evolve any volatile residues at the temperature range applied in these experiments. The samples were evacuated at room temperature down to about 10^{-4} Pa for 24 h, then activated under vacuum for 1 h at 473 K [7] and finally cooled down to pre-determined exposure temperature (in the present study 373 K). The above activation process was attributed to the desorption of chemisorbed hydroxyl groups from the thin oxidation overlayers coating the samples surfaces. These hydroxyls seemed to impede the dissociative chemisorptions of H_2 on the surface leading to a reduced flux of the H atoms into the sample. Ultra-pure hydrogen produced by heating a uranium hydride bed was admitted to the chamber, at the desired pressure (in the range 6×10^2 to 2×10^4 Pa).

Unlike GC's formation which is clearly displayed by the in situ optical microscope observations [1–7], the formation of the tiny sub-micron precipitates is not directly detected within magnification scales of HSM (magnification of up to ×50). In some cases the coloring of the surface is observed during this stage. However, when the sample is exposed to hydrogen for a longer period of time, formation of GC's starts to appear and the two types of "families" (i.e., GC's and the dense tiny precipitates indicated by some color changes of the space between the GC's) coexist on the surface, as demonstrated by Fig. 1.

In order to quantitatively specify the kinetics of the early precipitation stage, the duration of the exposures were usually limited to time periods shorter than those required for start of GC's formation. After reaching a pre-determined exposure time in the range 15–3×10^4 s, depending on the given pressure and temperature conditions, hydrogen was evacuated from the chamber, and the sample delivered to a higher magnification set-up (usually on Atomic Force Microscope, AFM and in some cases to a Scanning Electron Microscope (SEM) where the sub-micron characteristics of the precipitates were analyzed. Also, X-ray diffraction (XRD) measurements were performed on these samples.

3. Results and discussion

Fig. 2 demonstrates an AFM image of a sample exposed to 2×10^4 Pa of hydrogen (at 373 K) for 30 s. The very bright larger features are oxide inclusion which were initially present on the surface of the sample while the smaller spots (clustered densely) are the precipitated hydride nuclei. Some line height profiles taken across the hydrides are indicated in the figure (by (a) (b)) and illustrated on the right-hand side of the figure.

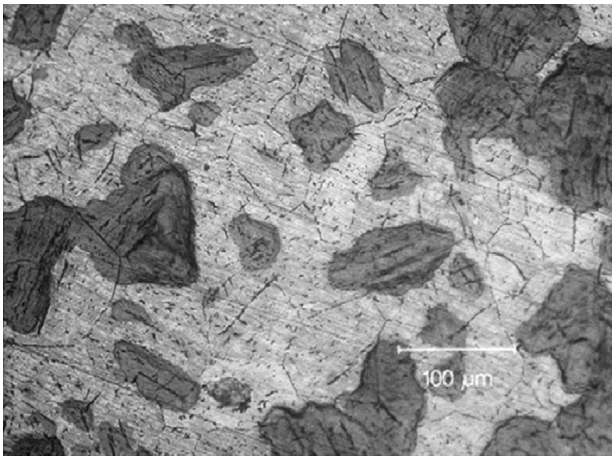

Fig. 1. Two types of "families" developed on the surface, GC's and dense tiny precipitates (indicated by the brightness of the grains).

Typical height scales of these spots are in the range of 0.05–0.20 μm. Due to overlapping of these densely clustered spots it is not possible in most cases to determine accurately their lateral size; however, it ranges in the higher sub-micrometric range, i.e., diameters of about 0.5–1 μm. The density number of the above hydride precipitates is actually not uniform and may vary for various grains orientations, as illustrated in Fig. 3. This variation in the precipitates densities is also indicated in Fig. 1 (a smaller magnification) by corresponding changes in the brightness of the different grains.

As discussed in [1,2], the nucleation of the above tiny "family" of hydride spots requires the penetration of H atoms across the surface oxidation layer and the build-up of a local H concentration at the oxide–metal interface that exceeds the thermodynamic solubility limit of the M–H system (at the given reaction temperature). Also, the stress fields that accompany such a nucleation and growth process (which takes place beneath the surface oxidation layer causing the compression of the formed hydride nuclei by the surrounding matrix) may impede the development of these precipitates. The observed variations of the precipitation densities of the hydride spots within various grains orientations may thus be either due to the different characteristics of the corresponding coating oxidation layers (e.g., thickness, surface properties, etc.) or due to the different stress fields that develop during the hydrides nucleation and growth.

Another possible reason for such differences in different metallic grains may arise from variations in the dislocations densities in these grains. It is apparent (e.g., in Fig. 3) that the precipitated hydride clusters have a certain preference to align along certain orientations, forming "streaks" of clustered hydride spots. These "lines" or "streaks" are actually not oriented along a fixed direction (even within a given grain). It is thus possible that the nucleation of the hydride initiates at some dislocation edges located at the metal–oxide interface [2], forming the above aligned structures. As different grains may possess different dislocation densities, this may also account for the observed variations in the hydrides clustering densities in the different grains.

A quantitative kinetic treatment of such nucleation and growth processes should actually require the determination of the time dependence (i.e., the kinetic function) of both, nucleation densities (i.e., number of precipitated nuclei per unit area) and growth rates (i.e., the dimensional changes of the precipitated nuclei) [1,2]. However, the clustering nature of the precipitation which leads to an overlapping of many adjacent nuclei, the very rapid kinetics of