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Hydride Formation of Rare Earths under Water Vapor

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Thin films of Gd were exposed to water vapor at 423°K for about 1 to 3 hr. X-Ray diffraction indicates that this treatment results in complete dihydride formation. No signs of oxide formation are evident in the X-ray diffraction patterns. The presence of oxide layers in materials prior to water vapor treatment appears to destroy the conditions which allow for hydride formation. This is concluded from similar experiments on fine particles of Er prepared by laser techniques.

Introduction

During studies of the influence of hydrogen on solid-state properties of intermetallics based on rare earths it became of interest to investigate hydriding as a result of exposure to water. It is well known (*1*) that certain electropositive elements (e.g., Zr, U) react with steam to form mixtures of hydrides and oxides in certain ranges of temperature. Intermetallic compounds based on electropositive elements can, therefore, be contaminated by hydrogen when, say during preparation or storage, these materials are exposed to water. In fact, it has been recently shown that exposure of thin films of Dy to steam around 430°K results in quantitative hydride formation while an analogous experiment on Nd yields predominantly oxides and hydrides (*2*). It became, therefore, of interest to study whether the process of hydride formation takes place in thin films of other rare-earth metals and in forms of the metals other than thin films. This is especially so as hydride formation from water vapor would allow a technologically interesting water-splitting cycle.

Experimental

Thin films of Gd were prepared by standard sputtering techniques onto glass slides, yielding films of approximately 10 000-Å thickness. The films were placed in a quartz tube under inert atmosphere and water vapor was passed over them at 420°K. The samples were removed at 45-min intervals. The films were analyzed by X-ray diffraction. Also reactions of bulk materials and fine particles in steam were studied on several rare earths. Fine particles of Y and Dy were obtained by cycles of hydrogen absorption and desorption. For these experiments Y and Dy were hydrided under 30 atm hydrogen at 570°K. The hydride was then transferred into the quartz tube of the water vapor treatment apparatus and the tube was evacuated to approximately 10 μm and then brought to 1170°K for 15 to 30 min. This procedure resulted in complete desorption of the hydrogen, yielding finely powdered materials (of order 50-μm particle size). For water vapor exposure, the desorbed material was allowed to cool in the reaction tube under vacuum, then water vapor was

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introduced under near atmospheric pressure into the tube for varying amounts of time. A number of experiments were performed at temperatures ranging from 420 to 570°K. An experiment was also performed on DyH_2, desorbed from DyH_3, exposing the material to water vapor at 420°K for 2 hr.

Also, a second method for the preparation of fine powders was employed using laser techniques as outlined in more detail elsewhere (*3*). For these studies Er was chosen in view of the relative ease, in this case, of distinguishing between hydrides and oxides via X-ray diffraction. Fine particles of Er were produced by exposure to laser pulses under Ar. Particles were collected on gold transmission electron microscope grids. Electron microscopy revealed the average particle size to be 300 Å in diameter. The gold grids containing the fine Er particles were exposed to water vapor at 420°K for 45, 90, 135, and 180 min. After subsequent cooling to room temperature, the samples were analyzed by electron diffraction.

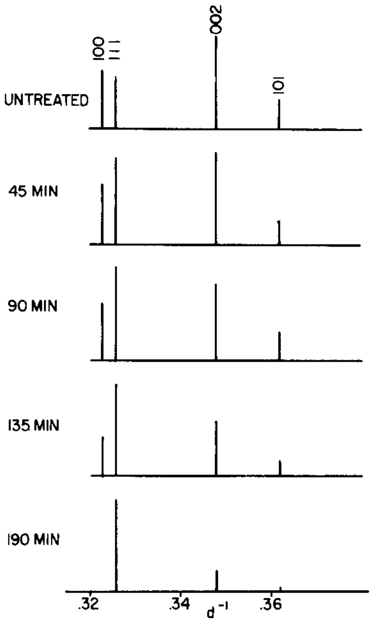

FIG. 1. Intensities of X-ray diffraction peaks, plotted vs d^{-1}, of a Gd thin film exposed to water vapor for varying amounts of time. Peaks designated (100), (002), and (101) correspond to Gd, while (111) corresponds to GdH_2.

Results and Discussion

The X-ray diffraction patterns of thin films of Gd exposed to water vapor are shown in Fig. 1. Virtually complete dihydride formation has occurred after 180 min at 423°K. Only a small amount of Gd metal (5%) and no oxide appears in the diffraction pattern. The lattice constant of the hydride is $a_0 =$ 5.297 Å, in good agreement with $a_0 =$ 5.303 Å, reported in the literature (*4*). (The diffraction pattern corresponds to one of GdH_2 prepared in this laboratory by conventional methods.) It should be stated that the untreated film already showed small amounts of the dihydride (about 10%), most likely due to the reaction of Gd with water vapor in the air. This corroborates the findings of Dexpert-Ghys *et al.* (*2*) who also observed the reaction of thin films of Dy with water vapor in the air. Our Gd films were exposed to air for approximately 4 weeks before water vapor treatments were begun.

Exposure of bulk materials to boiling water results in partial oxide formation after long periods of time (about 24 hr). Shorter exposure times do not produce noticeable changes in the X-ray diffraction patterns. X-Ray diffraction studies of powders of Y and Dy, prepared by desorption of the hydrides, show complete desorption to have occurred. However, evidence of small amounts of cubic oxide is found in both cases. Water vapor treatments at temperatures less than 473°K result in no reaction. Treatments above 470°K yield an increase of oxide formation in addition to small amounts of dihydride. No reaction occurs with DyH_2 at 420°K. Similar findings were made on fine particles of Er obtained by laser evaporation. Electron diffraction of erbium prepared in this way gives evidence of small amounts of cubic oxide. Diffraction patterns of the materials exposed to water vapor at 423°K show no change from the untreated materials.

The results taken at face value suggest that some rare earth in the form of thin films are capable of a water-splitting reaction whereby a hydride is formed while oxygen is assumed to be liberated. The thermodynamics for this reaction have been outlined earlier (*2*). Accordingly, hydride formation from water is thermodynamically feasible under the experimental conditions, however, the competing oxide formation should be energetically favored. The absence of oxide formation in a certain range of temperature, therefore, indicates kinetics control of the reaction. It should be mentioned at this point, however, that there is thus far no unequivocal evidence for the absence of oxide formation. In principle an amorphous oxide or hydroxide could have escaped detection by the diffraction experiments mentioned. The fact that hydroxide or oxide formation becomes easily detectable at slightly higher temperatures, together with its occurrence in the case of Nd, makes this, nevertheless an unlikely possibility.

The failure of hydride formation under steam found for the fine particles obtained in this study by hydride decomposition of Dy or Er (or laser evaporation in the case of Er) compared to the evidence for hydride formation in thin films of Gd or Dy may be explained by the presence or absence, respectively, of surface oxide layers. One might expect that fine particles of some of the rare earths with purified surfaces will have similar properties with respect to water splitting as the thin films of the same materials. The differences observed might be ascribed to the fact that bulk specimens are relatively immune to contamination by hydrogen. Nevertheless, considerable care during preparation and subsequent storage of intermetallics based on rare earth has obviously to be exercised in order to assure that no contamination by H occurs.

From the success of quantitative metal hydride formation under steam it would appear that a technologically interesting water-splitting process may be developed if materials based on electropositive elements can be prepared in large quantities with reactive surfaces. Further studies in this direction on related materials including intermetallic compounds composed of electropositive elements will be reported at a later date.

Acknowledgment

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