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Rare Earth Hydrides Formed by Reaction of Rare Earth Metals with Water Vapor*

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The reaction of Pr, Gd, Dy, and Er with water vapor has been studied in the temperature interval 100 to 140°C. There was corroboration of the earlier observations of J. Dexpert–Ghys, *et al.* (*J. Less Common Metals*, **41**, 105, 1975) to the effect that (1) DyH_2 forms when Dy is treated with water vapor and (2) there is no evidence by X-ray diffraction of the formation of $Dy(OH)_3$ and Dy_2O_3. Since the free energy change involved in forming DyH_2 and O_2 from Dy and H_2O is about +17 kcal, the reaction was carried out under radiation in an effort to ascertain whether the missing energy was being photochemically supplied. Results were negative. Mass spectrometric examinations of the reacting system using O^{18}-enriched water showed no oxygen in the gaseous products. Study of the solid using Auger spectroscopy gave clear indication of large amounts of oxygen in the sample after reaction with water. Presumably the incorporation of oxygen in the lattice permits the thermodynamic requirements to be satisfied. Oxygen is not present in Dy in a phase with sufficient long-range order to give a detectable X-ray diffraction pattern. Pr and Gd in the form of filings react with H_2O to give dihydride and hydroxide. Er is unreactive as judged from X-ray diffraction measurements.

Introduction

The behavior of thin films of Nd and Dy in the presence of water vapor has recently been examined by Dexpert-Ghys *et al.* (*1*). They found that Dy in the form of films approximately 2000 Å thick is transformed into DyH_2 upon exposure to water vapor at 140°C. The DyH_2 was identified by X-ray diffraction. No evidence for oxide formation was observed under these conditions. In contrast, thin films of Nd upon prolonged exposure to water vapor under the same conditions were transformed largely into $Nd(OH)_3$, also identified by X-ray diffraction.

If, in the reaction between water vapor and Dy, the oxygen is not present as an oxide or a hydroxide in the reaction products, it must be presumed that it is liberated as gaseous oxygen, according to the equation

$$Dy + H_2O(g) \rightarrow DyH_2 + \tfrac{1}{2}O_2. \qquad (1)$$

If this indeed occurs it is very interesting because of its bearing upon water splitting. Reaction of Dy in thin layer form with water to form DyH_2 and liberate oxygen would provide a means to split H_2O. The hydride could be decomposed at elevated temperatures to restore the Dy film and release H_2 after which the Dy could be reused.

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The process of Eq. (1) appears to be rather unlikely from the standpoint of thermodynamics unless important factors are to be accounted for. The free energy of formation of DyH_2 is -36.0 kcal/mole. Using this we obtain the value $+17$ kcal for the free energy change for reaction (1). It is thus clear that the reaction cannot proceed spontaneously unless energy is supplied simultaneously by some other process.

Of the possible additional energy sources, two warrant consideration. It has been suggested[1] that surface contributions may be sufficiently important to render the thermodynamics favorable. We do not feel that this is likely. With a reasonable upper limit for surface tensions (500 dyne/cm) and areas (< 0.1 m^2/g)[2] this could not contribute more than 0.01 kcal/mole. Another possibility is that the missing energy might be supplied photochemically. The present study was initiated partly to test this hypothesis and partly to ascertain whether the observations of Dexpert-Ghys *et al.* could be corroborated. Initially, Dy in the form of thin films was studied with respect to its reactivity with water vapor and the observations of the French workers were confirmed. The investigation was then broadened in two ways: (i) To include an evaluation of photochemical factors in the reaction of Dy thin films with H_2O and (ii) to study the reaction of filings of Pr, Gd, Dy, and Er with water vapor.

It should be noted that the results obtained by Dexpert-Ghys *et al.* in which $Nd(OH)_3$ was formed are consistent with thermodynamics. ΔG for the reaction of Nd with H_2O to form the hydroxide and H_2 is negative to the extent of 149 kcal per mole of $Nd(OH)_3$ formed.[3]

Since Dexpert-Ghys *et al.* observed hydride formation for Dy films, this element was examined in the present study in thin film form. In addition, Pr, Gd, Dy, and Er were examined in the present study in the form of fine powder. The purpose of this paper is to present information concerning the nature of the reaction products. The experimental methods employed include X-ray diffraction, Auger spectroscopy, and mass spectroscopy.

Experimental

The powders were obtained by filing the lanthanide ingots (stated purity 99.9%) in argon atmosphere. The filings were then passed through a 270-mesh sieve and pressed into indentations in Plexiglas slides for treatment with water vapor and for X-ray diffraction analysis. The dysprosium films were formed on glass slides (1 × 3 in.) by vapor deposition. The dysprosium was vaporized by heating the sample to the melting point in a tantalum boat at pressures of about 10^{-8} Torr. Ellipsometry measurements (*3*) indicated that the films thus obtained were of thicknesses ranging from 2000 to 2500 Å.

The reaction with water vapor was brought about by positioning the slides in a glass tube through which a mixture of helium and water vapor was passed. The portion of the tube in which the sample was placed was maintained at fixed temperatures ranging from 100 to 140°C. The helium, before passing into the system, was bubbled through water, the temperature of which was controlled to bring the partial pressure of water to about 40 Torr.

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[1] P. Caro, private communication to W. E. Wallace.

[2] See, for example, the surface areas of pulverized rare earth alloys determined by A. Elattar and W. E. Wallace, *Science*, submitted for publication.

[3] The ΔG of formation of $Nd(OH)_3$ was taken from Circular of the National Bureau of Standards 500, "Selected Values of Chemical Thermodynamic Properties," issued February 1, 1952.

All X-ray diffraction analyses were carried out with a Diano XRD-6 diffractometer with Co$K\alpha$ radiation. X-Ray patterns were obtained for the samples before and after exposure to water. The rare earth metals examined in this investigation all have hexagonal crystal structures, whereas the hydrides are cubic. The X-ray patterns could therefore be used readily to monitor the formation of the hydride phase. The DyH_2 (111) and (200) peaks were the main ones used to show the presence of DyH_2. Each pattern was also examined for any evidence of R_2O_3 or $R(OH)_3$ formation.

A Varian Auger–LEED spectrometer was employed to obtain the depth profile of oxygen in the dysprosium films which had been exposed to water for different lengths of time. Various depths were examined by sputtering the metal with argon beams. The primary beam energy used for all analyses was 2000 eV. A quantitative estimation of the amount of oxygen at different depths in the dysprosium was made by comparing the ratios of heights of peaks corresponding to oxygen and dysprosium at a certain depth to the corresponding ratio in a sample of Dy_2O_3.

To detect the formation of O_2 from the reaction of dysprosium with water a sealed glass system was used. This consisted of an ampoule to contain the slides bearing the dysprosium films, a U-trap, and a closed-tube mercury manometer. The system was designed for minimal dead space, estimated to be less than 10 cm^3. When an experiment was carried out, 15 to 20 cm^2 of glass slides bearing the Dy film were introduced into the ampoule and about 0.1 cm^3 of water, enriched to the extent of 20% with H_2O^{18}, was added to the system. The water was frozen in the trap with dry ice and the system was then evacuated and sealed off. The trap was warmed up to evaporate the water and the reaction was allowed to proceed. The sample was irradiated with a xenon lamp during this period. To detect O_2 or H_2 which might have been released during the reaction, the remaining water was condensed in the trap and frozen with solid CO_2, whereupon the presence of any gas not condensed at this temperature was indicated by the pressure reading on the built-in closed-tube manometer. The noncondensable gas pressure was determined in this manner both before and after the exposure of the sample to water vapor. Pressures were read to 0.02 Torr with a cathetometer. After the conclusion of the experiment, the portion of the system consisting of the ampoule (which included most of the dead space) was sealed off and separated from the rest of the system. It was then transferred to a crushing chamber which was attached to an LKB-9000 mass spectrometer where the composition of the gas was determined.

Results and Discussion

Dysprosium in thin film form and in the form of filings was exposed to water vapor 140°C for a 4-day period. Films and filings were free of a hydride phase, as evidenced by the X-ray diffraction measurements. The only reaction product observed was DyH_2. No indication of Dy_2O_3 or $Dy(OH)_3$ was seen in the X-ray patterns with either the thin films or the powder. The results of Dexpert-Ghys *et al.* were thus confirmed. The Dy system was examined after having been exposed to radiation from a xenon lamp while in contact with water vapor. The radiation was without effect.

Results obtained with the several rare earth elements studied are summarized in Table I. The behavior of Pr and Gd is consistent with the observations of Dexpert-Ghys *et al.* for Nd.

Since X-ray diffraction gave no indication of an oxygenated solid phase, experiments were undertaken to determine if gaseous oxygen was produced in the reaction, using

TABLE I

EXPERIMENTAL CONDITIONS AND REACTION PRODUCTS

Metal		Exposure time[a] (hr)	Exposure temperature[a] (°C)	Products
Pr	Powder	36	100	$Pr(OH)_3$, PrH_2 (trace)
Gd	Powder	31	140	$Gd(OH)_3$, GdH_2
Dy	Powder	100	140	DyH_2
Dy	Thin film	~20	140	DyH_2, DyO_x[b]
Er	Powder	100	140	No reaction[c]

[a] The samples were exposed to water vapor at a partial pressure of 40 Torr.

[b] Results obtained by Auger spectrometry whereas the other data in this column were acquired by X-ray diffraction. "DyO_x" could also be amorphous $Dy(OH)_3$.

[c] As evidenced by X-ray diffraction.

water enriched with O^{18} and the apparatus and procedure described above. After 10 hr exposure to water vapor at 15–40 Torr and at a temperature in the range of 90–145°C an increase of 0.60 mm was observed on the manometer. This corresponds to about 2.0×10^{18} molecules of H_2 and/or O_2. Mass spectroscopy analysis of the gas showed a high concentration of hydrogen. At the same time, no increase above background was observed in the amount of diatomic oxygen with a mass to charge ratio of 34 (corresponding to $O^{16}O^{18}$, the most probable heavy oxygen species). It is therefore inferred that no gaseous oxygen is formed in the reaction.

Since the oxygen is not in the gas phase it is clear that it must be in the solid but in a form not detectable by X-ray diffraction. The films of Dy which had reacted with water were accordingly examined by Auger spectroscopy (AES). Results of these analyses are shown in Figs 1 and 2. A depth profile (Fig. 1) revealed that a large amount of oxygen is present in the exposed dysprosium thin films. An increase in the water exposure time yielded an increase in the oxygen concentration in the films (Fig. 2). Quantitative calculations of the oxygen content of the film samples exposed for an extended period (> 1

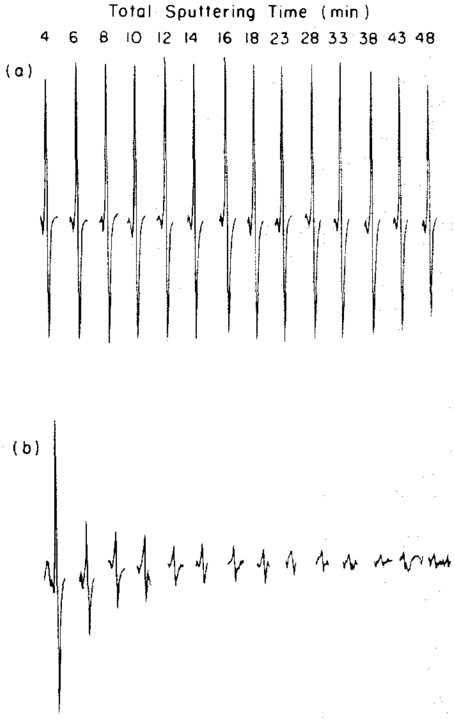

FIG. 1. A comparison of the 510-eV oxygen peak heights at different dysprosium film depths for (a) a water-treated dysprosium film sample (exposed 22 hr) and (b) an untreated dysprosium film sample. Sputtering was accomplished using argon ions produced by a 3-keV ion gun at an argon residual pressure of about 4.5×10^{-5} Torr. For dysprosium films, this yields a sputtering rate of approximately 30 Å/min.

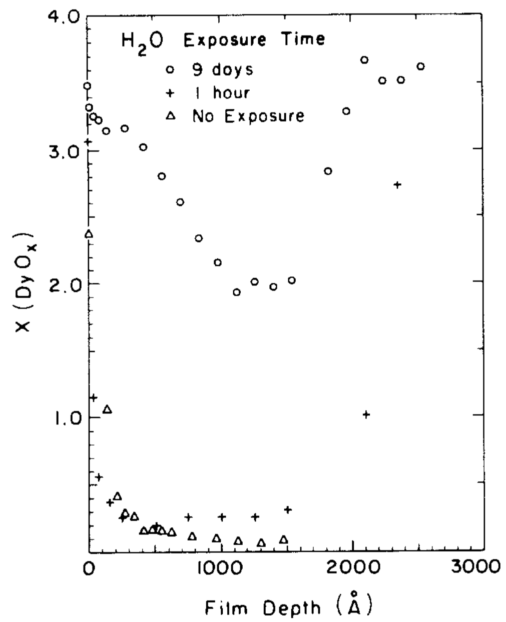

FIG. 2. Oxygen concentration depth profile of dysprosium thin films which had been exposed to water for different lengths of time.

week) indicated oxygen concentrations exceeding 60 at%. The rise in oxygen content at depth exceeding 1500 Å is due to the underlying glass plate.

It is apparent from the combined X-ray and AES results that the dysprosium oxide and/or hydroxide is initially amorphous. It is also clear that the reaction involved is not a photocatalytic dissolution of water into diatomic hydrogen and oxygen, but rather an ordinary metal–water reaction yielding the metal oxide and hydrogen with some of the latter reacting with the rare earth metal to form hydride. The oxide, or hydroxide, formation provides the driving force for the reaction and the overall process because of the exothermal nature of oxide, or hydroxide, formation is not contrary to thermodynamic requirements.

It is to be noted that after prolonged exposure to water vapor the dysprosium films show an oxygen content as detected by AES which actually exceeds that in Dy_2O_3 (Fig. 2). There are three possible features of the system experimental methodology which could lead to this surprising behavior: (i) Migration of the oxygen from within the films to the surface caused by localized heating from the argon sputtering beam; (ii) Reimplantation of sputtered oxygen atoms by the argon beam; (iii) The presence of $Dy(OH)_3$. Of these, the latter seems more likely.

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