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CALORIMETRIC MEASUREMENTS IN THE Gd/H_2 SYSTEM AT ROOM TEMPERATURE

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ABSTRACT

The heat produced by hydrogen successively dosed to vacuum-deposited films of gadolinium was measured in a calorimeter at room temperature. The first doses of hydrogen gave relatively low heats which could be ascribed to the formation of the solid solution phase. At an H/Gd ratio of about 0.1–0.2, the heat corresponding to the formation of the dihydride was obtained. When the H/Gd ratio exceeded approximately 1.4, a gradual decrease in heat, and a deceleration of its production were observed. At H/Gd $\gtrsim 2$ the heat was produced too slowly to be measured in the calorimeter used. A comparison of the found behavior with the literature data is presented and an explanation suggested.

INTRODUCTION

The interaction of hydrogen with lanthanide metals is generally well understood [1,2]. Hydrogen molecules dissociate on the lanthanide surface into atoms which move rapidly into the bulk, overcoming the low potential barriers between the equilibrium sites. The solid solution thus formed is far from an ideal one and tends to form clusters. At a sufficiently high hydrogen concentration, an ordered dihydride phase begins to segregate. This is accompanied by a change of the lattice, in most lanthanides from a HCP to a fluorite type with an FCC metal sublattice. A two-phase system appears, in which an ordered and a disordered (solid solution) phase coexist. The equilibrium hydrogen pressure remains constant over the two-phase range. Hydrogen atoms, however, can also penetrate into the less accessible interstitial sites in the dihydride lattice, and the hydrogen pressure therefore again begins to increase before the stoichiometric composition (MH_2) has been reached. At the formal MH_2 composition, the same number of sites in the dihydride lattice remains vacant as those of the interstitial sites are filled. The latter sites mostly eventually transform into a trihydride lattice, either with or without a change of the dihydride lattice; only Yb and Eu do not form trihydrides. From the viewpoint of the kinetics it is clear that with

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increasing temperature, the range of the solid solution shifts to higher hydrogen-to-metal ratios (easier declustering), while the filling of the interstitial sites in the dihydride lattice sets on sooner. Consequently, a narrowing of the range occurs in which a solid solution can coexist with the dihydride lattice, without any marked admixture of occupied dihydride interstitial sites. This manifests itself by a narrowing of the range of the constant equilibrium pressure as the temperature increases.

The heats of dissociative dissolution of hydrogen in the lanthanide metals and of formation of their dihydrides and trihydrides have been foremostly estimated from the temperature dependence of the equilibrium hydrogen pressure. Arrhenius plots of ln p vs. $1/T$ have then yielded the enthalpy and entropy values of the processes involved. It should be noted that the Arrhenius plot gives the heat effect for the formation of dihydride from the saturated solid solution, not from the pure metal. Although well known [3–5], this has sometimes been neglected with the reference to but a small difference arising when the two initial states are used. How far such a standpoint is justified can be demonstrated on the holmium–hydrogen system [4]. In the temperature range 820–870 K, the solid solution was saturated at the H/Ho ratio of about 0.40, and the hydrogen pressure began to increase at H/Ho $\approx$ 1.85. In order to obtain the heat of formation of the deficient dihydride from gaseous hydrogen and pure metal, it is necessary to integrate the partial heats up to the saturated solution and to add the heat determined for the two-phase range. From the tabulated data for Ho [4], the average heat of solution in the one-phase region was estimated to be 181 kJ mol^{-1} H_2, and the Arrhenius plot gave 221.2 kJ mol^{-1} H_2 for the formation of the dihydride. Hence, the required true heat of formation of $HoH_{1.85}$ is $\frac{1}{2}[0.4 \times 181 + (185{-}0.4) \times 221.2] = 196.6$ kJ mol^{-1} $HoH_{1.85}$. The recalculation for 1 mole of the reacted hydrogen gives $196.6 \times (2/1.85) = 212.5$ kJ mol^{-1} H_2. This is but some 4% less than the value obtained when starting with the saturated solution.

To fill the lack of data from direct measurements of the heat of formation of dihydride at room temperature, we have undertaken calorimetric experiments on vacuum-deposited films of several lanthanides. The introductory results for five metals have been reported previously [6]. The present communication deals with somewhat more detailed measurements on gadolinium, aimed primarily at proving that the heat of dissolution of hydrogen in the metal is also lower at room temperature than the heat of dihydride formation, at least by the amount needed for the rearrangement of the crystal lattice.

EXPERIMENTAL

The amount of absorbed hydrogen was measured in a glass volumetric adsorption apparatus [6]. The corresponding heat effect was determined by means of a calorimeter designed for work with materials in the form of films [7]. The calorimeter consisted essentially of a thin-walled glass tube (36 mm diameter) with a platinum thermometer and a calibration wire wound on its outer wall, sealed in a glass jacket. The films were deposited onto the inner wall of the tube thermostated at about 285 K, by evaporation of a small piece of gadolinium held in a tungsten loop in the axis of the calorimeter tube. Before and during the film deposition, the pressure in the calorimeter was of the order of 10^{-7} Pa (10^{-9} Torr). The films covered approximately 80 cm^2 of the wall, and their average thickness amounted to several tens of nanometers (hundreds of Ångstroms).

During the measurement, the calorimeter was thermostated at approximately 295 K. The calorimeter has been constructed for the measurement of rapid heat processes only, and can operate provided the heat transport via the gas phase above the film is negligible [8]. Therefore, hydrogen was dosed to the film in short pulses; the amount of gas in each pulse was determined by means of a McLeod manometer [9]. The heat produced by the individual hydrogen doses (typically about 5×10^{-2} J) was evaluated from the temperature–time trace on the recorder chart by a procedure outlined previously [10].

Gadolinium was prepared in the Institute of Metallurgy of the Academy of Sciences of U.S.S.R. and its claimed purity was 99.96%. Hydrogen (grade "Wasserstoff reinst") was the product of the Reinstgase des VEB Technische Gase Leipzig, G.D.R. Before admission into the measuring section of the apparatus, it was passed through freezing traps cooled to 77 K.

RESULTS AND DISCUSSION

Two experiments with gadolinium films were performed. Their characteristics are given in Table 1. The measured heats referred to 1 mol of consumed hydrogen are shown in Fig. 1. The heats obtained at very low H/Gd ratios were clearly lower than those in the next composition range. If

TABLE 1

Characteristics of the experiments

Experiment	A	B	C	D	E	F
1	5.3	25	3.6	4–9	180	772
2	3.7	15	2.7	3–5	232	599

A = film weight (mg); B = time of the film deposition (min); C = background pressure before the film deposition ($Pa \times 10^7$); D = pressure during the film deposition ($Pa \times 10^7$); E = time from the end of the film deposition to the first hydrogen dose; F = time from the end of the film deposition to the last hydrogen dose (min).

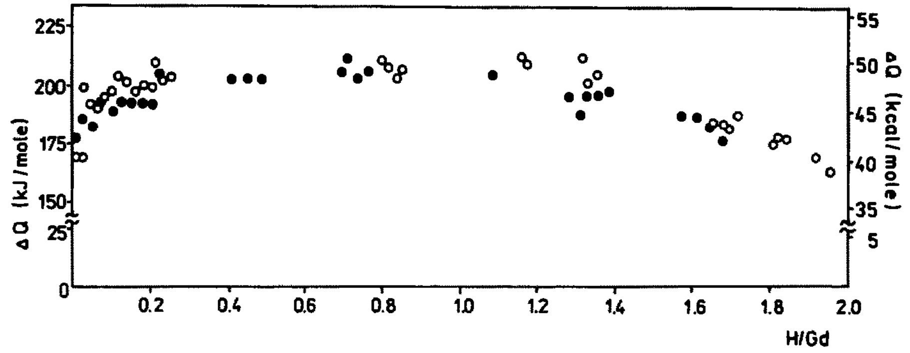

Fig. 1. Results of the heat measurement at 295 K on the Gd films 1 (○) and 2 (●).

these lower initial heats are omitted, the average heat of the two experiments amounts to 201.8 ± 1.1 kJ mol^{-1} (48.2 ± 0.3 kcal mol^{-1}).

The uptake of hydrogen by the films was very rapid up to an H/Gd ratio of around 1.4, as was evidenced by the shape of the temperature–time trace on the calorimeter recorder. At higher H/Gd ratios, the shape of the temperature–time traces began to show increasingly appreciable deceleration of the heat production on further hydrogen dosing. Interestingly, this was accompanied by a decrease of the evolved heat. Above a H/Gd ratio of about 2, the heat production continued, but it was too slow to be reliably determined in the calorimeter used.

McQuillan [5] presented Arrhenius plots for the solid solutions of hydrogen in Gd, and also in Tb, Dy and Lu, based on the measurements of the equilibrium hydrogen pressure between 830 and 1250 K for an H/Gd ratio between 0.017 and 0.4. The partial heat of solution of gaseous hydrogen increased from 125 to 170 kJ mol^{-1} in that composition range. The heat of formation of the non-stoichiometric dihydride from the primary hydrogen solution amounted to 204.4 kJ mol^{-1}. Similar values were published by other authors (Table 2). The difference between the highest heat of solution and the heat of formation of dihydride from the saturated solution essentially gives the heat of reorganization of the crystal lattice, increased by the heat effect due to the growing immobilization of the hydrogen atoms. For Gd, the heat of recrystallization of 204–167 = 37 kJ mol^{-1} can be read off from the graphs shown by McQuillan [5]. The corresponding value for Ho amounts to 23 kJ mol^{-1}, as follows from the data of ref. 4.

Our results show that, also with thin films at room temperature, the heats of hydrogen solution are lower than the heats of dihydride formation. It should be noted that in some chemisorption systems, the lower heat values obtained for the first one or two dôses in film calorimeters were considered as likely artifacts [7,15]. In the present case, however, the lower initial heat values are more reliably established and it is not plausible to explain them as an artifact due to a partial adsorption of hydrogen in cold traps or on the outgassed walls of the apparatus.

TABLE 2
Heat of formation, $-\Delta H_f$, of the non-stoichiometric gadolinium dihydride from the hydrogen equilibrium pressure

$-\Delta H_f$ (kJ mol^{-1} H_2)	Temp. range of the measurement (K)	Ref.
204.4	833–1248	5
196.0	873–1073	11
214.8	973–1273	12
188.9	798–1123	13
197.7	1073–1173	14
Average: 200.4 ± 3.9		

The scatter of the experimental points allows only a rough estimate that the difference between the last heat of solution and the heat of dihydride formation in our system does not exceed some 12 kJ mol^{-1} H_2, and the range of the solid solution reaches an H/Gd ratio of 0.2 at the most, compared to 23 kJ mol^{-1} H_2 and H/Gd 0.4 obtained with Gd above 800 K [5]. This appears to be reasonable. First, when the published shifts of the solid solution range with temperature above 820 K [11] are extrapolated down to room temperature, a limiting H/Gd ratio of around 0.1–0.2 is obtained, in agreement with our experimental finding. This may be accounted for by the decreasing tendency of hydrogen to leave the lattice positions as the temperature increases. Second, the lower heat of recrystallization found at room temperature may be explained by the decreased mobility of hydrogen atoms, resulting in a higher heat of solution which, thus, becomes closer to the heat of dihydride formation. In general, the narrow solid solution range and the small difference between the average heat of solution and the heat of dihydride formation may cause an apparent constancy of the heat effect of the hydrogen uptake from the very beginning, if less detailed measurements are performed [6].

The hitherto published heats and entropies of formation of gadolinium dihydride have been derived exclusively from the equilibrium data above 750 K. At lower temperatures, the equilibrium pressure of hydrogen is less than 10^{-2} Pa, making an exact measurement difficult and the attainment of equilibrium slow, particularly when compact pieces of metal are used. The heat of formation generally depends on temperature. The difference between its value at two temperatures is given by the heat capacity of the gaseous hydrogen and the difference of the heat capacities of the solid dihydride and solid metal. The former term being larger than the latter, a decrease in the heat of dihydride formation with falling temperature results. If the linear Arrhenius plot constructed from the data above 750 K is extrapolated down to 300 K, an equilibrium pressure of less than 10^{-20} Pa is obtained. The experimental work on Ce films at 300 K [16], however, gave an equilibrium pressure of about 10^{-4} Pa. This implies a sizeable curvature of the Arrhenius plot towards lower negative slopes, i.e., towards lower heats of dihydride formation at room temperature. This has actually been confirmed by calorimetric measurements at 295 K with Ce, Dy, Er, Tm and Lu [6] which gave values 6–14% lower than those calculated from the data at elevated temperatures. With Gd, however, there is no significant difference. This might be connected with the anomalously high specific heat of Gd, amounting to 0.30 J g^{-1} deg^{-1}, compared to some 0.15–0.17 J g^{-1} deg^{-1} with the other lanthanides. It is not a priori excluded that this anomaly also holds for the dihydrides.

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REFERENCES

1 W.M. Mueller, in W.M. Mueller, J.P. Blackledge and G.G. Libowitz (Eds.), Metal Hydrides, Academic Press, New York, 1968, Chap. 9.
2 G.G. Libowitz and A.J. Maeland, in K.A. Gschneidner, Jr. and L. Eyring (Eds.), Handbook of the Physics and Chemistry of Rare Earths, North-Holland, Amsterdam, 1979, Chap. 26.
3 C.E. Lundin, Trans. Metall. Soc. AIME, 242 (1968) 903.
4 F.C. Perkins and C.E. Lundin, J. Electrochem. Soc., 115 (1968) 21.
5 A.D. McQuillan, J. Less-Common Met., 49 (1976) 431.
6 O.A. Boeva, K.N. Zhavoronkova, M. Smutek and S. Černý, J. Less-Common Met., in press.
7 S. Černý, M. Smutek and F. Buzek, J. Catal., 38 (1975) 245.
8 S. Černý and V. Ponec, Catal. Rev., 2 (1968) 249.
9 S. Černý, V. Ponec and L. Hlådek, J. Catal., 5 (1966) 27.
10 M. Smutek and S. Černý, Collect. Czech. Chem. Commun., 44 (1979) 3425.
11 G.E. Sturdy and R.N.R. Mulford, J. Am. Chem. Soc., 78 (1956) 1083.
12 R.L. Beck, Rep. LAR-10, 1960, after P.M.S. Jones, J. Southall and K. Goodhead, AWRE Rep. No. 0-22/64, U.K. Atomic Energy Authority, Atomic Weapons Research Establishment, 1964.
13 P.M.S. Jones, P. Ellis and T. Aslett, AWRE Rep. No. 0-31/66, U.K. Atomic Energy Authority, Atomic Weapons Research Establishment, 1966.
14 G.G. Libowitz and J.G. Pack, J. Phys. Chem., 73 (1969) 2352.
15 S. Pålfi, W. Lisowski, M. Smutek and S. Černý, J. Catal., 88 (1984) 300.
16 G. Atkinson, S. Coldrick, J.P. Murphy and N. Taylor, J. Less-Common Met., 49 (1976) 439.