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Abstract

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On the Interaction of Cerium with Hydrogen

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Metallic cerium, when heated in an atmosphere of hydrogen to 250-300°, begins vigorously to absorb hydrogen with the formation of a hydride of variable composition ([1]-[3]).

The question of the existence of cerium hydride of stoichiometric composition CeH_2 was raised in 1913 by I. I. Zhukov ([4],[5]) on the basis of a study of the dissociation elasticity curve of the hydride. Subsequently, the existence of CeH_2 hydride was confirmed by calorimetric studies by K. Dialer ([6],[7]). In addition, in these latter works, for mischmetal—an alloy of rare earths containing about 50% Ce ([6])—and also for pure cerium ([7]), a hydride of composition CeH_3 was obtained.

In our work, cerium obtained from the Institute of Rare Metals was used as the starting metal; according to spectral analysis it contained 97% Ce and 2.9% Nd and Pr. Determination of the amount of hydrogen bound with cerium was carried out in parallel by three methods: 1) by the amount of hydrogen absorbed (pressure drop in the system), 2) by the gain in weight of the metallic cerium sample, and 3) by the volume of hydrogen evolved upon dissolving the hydride in dilute hydrochloric acid. The accuracy of the determination was $±$2% of the quantity being determined.

To carry out the hydriding, a metal sample weighing 0.1-3 g, carefully cleaned on the surface in a strong stream of dry carbon dioxide, was placed in a quartz tube connected to a vacuum system. After evacuation by a diffusion pump to 10^{-4} mm Hg, a furnace was moved over the tube, the temperature of which was maintained with an accuracy of $±$5°.

After 5 min, hydrogen carefully purified from oxygen and water vapor was introduced into the system, and the pressure drop was measured with a mercury manometer. After absorption had ceased, the excess hydrogen was pumped off and the product was cooled in vacuum to room temperature. In order to avoid ignition of the hydride on contact with air, the hydride was removed in a stream of dried carbon dioxide.

In carrying out the hydriding it was found, in contrast to literature data ([2],[3],[8]), that, provided the starting materials were thoroughly purified, hydriding of cerium occurs at room temperature without preliminary thermal treatment of

Fig. 1. Isotherms of hydrogen absorption by cerium

Figure 1: Fig. 1. Isotherms of hydrogen absorption by cerium

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

the sample. The composition of the resulting product varies within the limits CeH_3–$CeH_{3\cdot16}$. By hydriding cerium at elevated pressure (up to 14 atm.) it was established that the composition of cerium hydride does not depend on the hydrogen pressure.

Construction of diagrams "hydriding time–hydrogen pressure drop" (Fig. 1) showed a different character of hydrogen absorption in different temperature intervals. At low temperatures, hydriding proceeds with a noticeable induction period, which disappears above 200°. Figure 2 shows the curve of the dependence of hydriding time (to saturation) on temperature for identical cerium samples. Up to 200° and above

at 700° the rate of hydriding, in contrast to the interval 300–600°, increases with increasing temperature.

The dependence of the composition of cerium hydride on temperature was studied under two different experimental regimes. Under the condition of pumping off the excess hydrogen after saturation of cerium at each given temperature (Fig. 3,

Fig. 1. Isotherms of hydrogen absorption by cerium

curve 1), the form of the saturation curve is close to that of curve 2, obtained by Sieverts and Roell under the same conditions ([3]). The experiments forming the basis of curve 3 were carried out by heating a specimen of composition CeH_3 at specified

Fig. 2. Time of hydrogen absorption by cerium
Fig. 3. Dependence of the composition of cerium hydride on temperature

temperatures until equilibrium was established. The composition of the final product was calculated from the volume of the gas evolved. The form of curve 3 differs sharply from that of curves 1 and 2: two horizontal plateaus are clearly observed on it, corresponding to the compositions CeH_3 and CeH_2. In this case the temperature regions of their existence correspond to the descending branches of the curve in Fig. 2, i.e., the rate of formation of these hydrides increases with increasing temperature. At the same time, the formation of hydrides of variable composition (300–700°) is accompanied by a decrease in the reaction rate with increasing temperature, which is possibly connected with the dissolution of hydrogen in CeH_2.

The data of the present work make it possible to conclude that:

1. Hydriding of metallic cerium, under conditions of thorough purification of the starting substances, occurs at room temperature without preliminary heat treatment of the cerium sample.
2. When hydrogen is absorbed by cerium at room temperature (14–21°), irrespective of the hydrogen pressure, a hydride of composition CeH_3—$CeH_{3.16}$ is obtained.
3. The curve of the dependence of hydride composition on temperature and the curves of the hydriding rate confirm the formation of definite hydrides CeH_2 and CeH_3 and the presence of a phase of variable composition between CeH_2 and $CeH_{3.16}$.

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