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1961

SovietRxiv

Abstract

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CHEMISTRY

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ON THE HYDRIDING OF CERIUM-MAGNESIUM ALLOYS

(Presented by Academician I. I. Chernyaev, 29 IV 1961)

The absorption of hydrogen by cerium-magnesium alloys was established by Sieverts and Roell [1]. The authors state that the absorption capacity of cerium, 214 cm^3/g, is practically unchanged by the addition of small amounts of magnesium: alloys with 5.3 and 12.5% Mg, when cooled in an atmosphere of hydrogen, bind, respectively, 165.0 and 190.1 cm^3 of hydrogen per 1 g of cerium.

Recently the existence of cerium hydrides of composition CeH_2 and CeH_3 (hydrogen absorption 160 and 240 cm^3, respectively), obtained by the reaction of metallic cerium with hydrogen at room temperature, has been proved [2,3]. Both of these hydrides are unstable in moist air, especially CeH_3 [4]. By the reaction of metallic magnesium with hydrogen, magnesium hydride has been obtained in the form of a white powder, relatively stable toward moisture and air [5]. However, the hydriding of magnesium requires the use of elevated temperatures, pressure, and special catalysts.

On the basis of successful experiments in obtaining cerium and magnesium hydrides of constant composition, we carried out the hydriding of cerium-magnesium alloys over a wider range of magnesium concentrations than had been done by Sieverts and Roell. As starting materials we used cerium containing 97.75% Ce, 0.75% Nd, 0.4% Pr, 1.0% La, and 0.05% Fe, and refined magnesium with a content of the principal metal of not less than 99.9%. Alloys with a content of up to 85 at.% Mg were prepared by fusing weighed portions of metallic cerium with a master alloy corresponding to the composition of the compound Mg_3Ce (34.24% Mg) in corundum crucibles under a layer of LiCl—KCl flux (53.9 wt.% LiCl).

Hydriding was carried out at room temperature and a hydrogen pressure of 0.5-1 atm in the apparatus used for hydriding cerium [3]. Alloy samples were used both as-cast and after preliminary heat treatment, which noticeably accelerated the absorption of hydrogen.

The hydrogen content in the hydrided alloys was determined by measuring the volume released from a weighed portion of the substance upon its interaction with hydrochloric acid. The absorption of hydrogen by the alloys occurs with a variable induction period, which increases considerably as the magnesium content in the alloy is increased. Samples 13, 14, and 15 could be hydrided only after activation by preliminary heating.

It should be noted, however, that in the change in the duration of the induction period, the time of hydriding, and the magnitude of the absorption of the alloys, no strict regularity is observed with change in composition (Table 1, Fig. 1). This is apparently associated with the great sensitivity of these properties to changes in the structure of the solid alloys according to the cerium–magnesium phase diagram. The hydriding of alloys with a magnesium content greater than 30% is accompanied by cracking of the initially taken pieces along cleavage planes into regular rectangular black formations with a luster, brittle and easily ground into a fine powder.

Table 1

Composition of the products of hydrogenation of cerium–magnesium alloys

Experiment no.	Mg, at.%	Mg, wt.%	Induction period, min	Duration of hydrogenation	Hydrogen content per 1 g of hydride, ml	Hydrogen content per 1 g of cerium, ml	Hydrogen content, at.%	Hydride formula
1	0	0	1-3	1-4 min	234.9	240.0	75	CeH_3
2	0.1	0.002	90	2.0 h	233.2	238.9	74.79	$CeMg_{0\cdot0011}H_{2\cdot97}$
3	0.2	0.004	35	2.0 h	232.7	237.6	74.77	$CeMg_{0\cdot00218}H_{2\cdot98}$
4	0.5	0.10	10	>6 h	233.5	237.5	74.76	$CeMg_{0\cdot0059}H_{2\cdot98}$
5	1.0	0.18	15	2.5 h	233.5	238.9	74.68	$CeMg_{0\cdot01039}H_{2\cdot99}$
6	5.0	0.90	180	>6 h	237.3	241.2	74.48	$CeMg_{0\cdot052}H_{3\cdot07}$
7	10.0	1.89	>240	>6 h	242.0	251.0	74.41	$CeMg_{0\cdot111}H_{3\cdot23}$
8	20.0	4.15	>240	>6 h	240.6	256.8	72.11	$CeMg_{0\cdot249}H_{3\cdot23}$
9	30.0	6.92	>240	>6 h	282.4	319.6	72.97	$CeMg_{0\cdot43}H_{3\cdot86}$
10	35.0	8.55	20	>6 h	288.8	329.3	72.52	$CeMg_{0\cdot538}H_{4\cdot060}$
11	40.0	10.37	>240	>6 h	302.4	347.2	72.90	$CeMg_{0\cdot665}H_{4\cdot48}$
12	46.0	12.88	>180	>1.5 days	315.0	366.4	71.66	$CeMg_{0\cdot852}H_{4\cdot682}$
13	50.0	14.79	>240*	>6 h	272.8	341.5	67.37	$CeMgH_{4\cdot13}$
14	60.0	20.58	10*	>6 h	320.2	414.8	67.17	$CeMg_{1\cdot493}H_{5\cdot10}$
15	66.66	25.77	40*	~2 h	284.6	393.4	61.98	$CeMg_2H_{4\cdot89}$
16	75.0	34.24	Does not hydrogenate	Does not hydrogenate				

* After thermal treatment at 400°.

As is seen from the hydrogenation data (Table 1), small additions of magnesium to cerium (up to 5 at.%) introduce almost no changes in the composition of cerium hydride and are reflected only in a considerable increase in the induction period and in the time of hydrogenation. Hydrogenation of alloys containing more than 5 at.% magnesium proceeds with an even longer induction period; as a rule, hydrogen absorption does not begin within 6 h, and for alloys with 46-66 at.% Mg saturation is reached after several days. Large pieces of alloys of this composition do not hydrogenate at all, and they had to be comminuted.

Analysis of the composition of the hydrogenation products of cerium-magnesium alloys (Table 1) shows that, when magnesium is added to cerium up to 30 at.% Mg, the hydrogen content corresponding to complete hydrogenation of both magnesium and cerium is not reached. Beginning with 30 at.% Mg, the compositions of the hydrogenated alloys correspond to the highest absorption of hydrogen by each of the metals separately, i.e., for an alloy $Mg_{mCe}n$ the composition of the hydrogenation product is close to the formula $Mg_{mH_{2m}}Ce_{nH_{3n}}$. In particular, a cerium alloy with 46% Mg is close in composition to the "double hydride" $MgCeH_5$. Beginning with alloy 13 (50% Mg), hydrogen absorption falls sharply and ceases completely with the alloy corresponding to the formula Mg_3Ce (34.24 wt.% Mg).

Fig. 1. Magnitude of hydrogen absorption (cm^3/g) for cerium-magnesium alloys.

Comparing these results with the phase diagram of cerium-magnesium alloys (Fig. 1), the initial region of small influence of magnesium on the magnitude of cerium absorption should be associated with the formation of solid solutions of magnesium in cerium. The greatest absorption effects characterize alloys approaching in composition the compound MgCe (14.79 wt. % Mg). Peritectic reactions of formation of the compound MgCe from Mg_2Ce (25.77% Mg) and Mg_2Ce from Mg_3Ce reduce the absorption of hydrogen by the alloys. This applies to an even greater degree to alloys richer in magnesium, which at room temperature do not absorb hydrogen either in the initial or in the heat-treated state.

Cerium hydride CeH_3 readily ignites in air and vigorously liberates hydrogen with water (2-4). Magnesium hydride, judging from the literature data, is little sensitive to air and moisture (5,6). Cerium-magnesium alloys hydrided to saturation up to 5 at. % Mg behave analogously to cerium hydride, but beginning with 10 at. % Mg and above the hydrogenation products ignite in air only upon vigorous grinding, while above 30 at. % Mg they do not react with air and moisture at all.

During thermal decomposition of the hydrogenation products, hydrogen, as in the case of cerium hydride CeH_3, is evolved in several stages. For example, for an alloy with 46 at. % Mg, vigorous evolution of approximately $^{2}/_{5}$ of all the hydrogen is observed in the interval 350-420°, and the second stage of hydrogen evolution corresponds to the temperature interval 900-1050° C.

The work carried out is of interest in indicating the possibility of obtaining, by hydrogenation of cerium-magnesium alloys, mixtures $Mg_mH_{2m}Ce_nH_{3n}$, the composition of which in the limiting case can be expressed by the formula $MgCeH_5$. The character of hydrogenation of binary cerium-magnesium alloys differs from that for pure cerium and magnesium; likewise, the properties of the obtained "double hydrides" differ from the properties of each of the simple hydrides CeH_3 and MgH_2 taken separately. For example, metallic magnesium does not interact at all with hydrogen at room temperature, metallic cerium readily absorbs it, whereas cerium-magnesium alloys are completely hydrided at room temperature, although considerably more slowly than pure cerium. As the magnesium content in the alloy increases, the ability of the hydrogenation product to ignite in air—a property characteristic of cerium hydride—gradually decreases, and resistance to interaction with water—a property characteristic of magnesium hydride—increases.

Thus, the products of complete hydrogenation of cerium-magnesium alloys of approximate composition MgH_2CeH_3, or $MgCeH_5$, obtained by us occupy, in their properties, an intermediate position in comparison with their constituent simple hydrides CeH_3 and MgH_2.

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Received
24 IV 1961

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Note: Figure translations are in progress. See original paper for figures.