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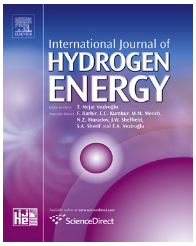

Selection of the hydrogen-sorbing material for hydrogen accumulators

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ABSTRACT

The hydrogen accumulation in metal hydrides is the urgent problem of hydrogen power engineering and the demand for metal hydrides as capacitive, safe and convenient in service sources of hydrogen has stimulated the study of hydrogen capacity of multicomponent alloys. In recent years, much attention has been given by scientists to the investigation of hydrogen-sorption and desorption properties of different materials, including nanocarbon structures and composites on their base, the study of peculiarities of the reversible hydrogen interaction with hydride forming metals and alloys, the development of high-pure hydrogen storage and transportation in solids. The present work is devoted to the development and methodology of selection of the chemical composition of metal hydride alloy for hydrogen accumulators.

Introduction

The world's research society has tried to use the hydrogen-sorption properties of different metals and alloys to solve a great variety of scientific and technical problems for over 50 years [1–9]. The properties of many chemical elements and their hydride alloys and compounds have been studied for this period. Metal hydrides have already found a wide application owing to the peculiarities of thermodynamics of hydrogen sorption and desorption processes that depend on the chemical composition of a solid subjected to the process of hydrogen pickup.

In recent years, much attention has been given to the development of hydrogen absorbing alloys due to their high hydrogen capacity. Under normal conditions, the amount of hydrogen stored in a vessel filled with metal hydride can be larger than that in the same vessel filled with liquid hydrogen. The method of hydrogen storage in solids advantageously differs from that in gas-cylinders and cryogenic. This method is safe and requires lower service costs. Therefore the world-known companies have put in order the serial production of

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various modifications of metal hydride accumulators of hydrogen.

The application of metal hydride technologies allows the manufacture of compact, safe and technologically flexible hydrogen treatment units. Also, peculiarities of the reversible hydrogen interaction with hydride forming metals and alloys makes it possible to purify hydrogen from gas admixtures in the MH units. The possibility to control the output hydrogen pressure by controlling heat influence on the MH sorbent allows the realization of controlled hydrogen supply to a consumer under the preset pressures. Storage purification, compression/controlled supply can be combined in a single multi-functional unit. This feature makes such applications extremely effective.

At present time, it has found applications both as the energy carrier and as the power source. If the change of electric current by moved hydrogen in pipe-lines is a rather complicated process, its transferring in containers of different construction has been put into operation firmly.

Selection of the hydrogen-sorbing material

The hydrogen storage alloy of AB_5 type ($B = Ni, Fe, Al$) prepared on the base of the commercial cerium ligature ($A = Ce, La, Pr, Nd$), lanthanum and nickel (both of technical purity grade) has been used in the unit. The composition of the alloy must provide a hydrogen equilibrium pressure of ~10 bar over MH at room temperature and above 150 bar at elevated temperatures.

For this purpose the chemical composition of the working alloy that would ensure the required characteristics of the unit has been computed and selected on the basis of the literature data on the binary constitution diagrams for Ce–La, La–Ni and Ce–Ni (Figs. 1–4). The ternary diagram has been computed and constructed for the Ce–La–Ni system (Fig. 5) (such diagram is unavailable in literature).

The following peculiarities have been considered in constructing the variant for a liquidus projection along the Mm-$LaNi_5$ section.

Ce–La constitution diagram

The Ce–La constitution diagram [10,11] is presented in Fig. 1. Thermal and microstructural analysis have revealed that δ, γ and β modifications of Ce and La form the continuous sequences of solid solutions [12–14]. The measured lattice parameters [13] have supported the conclusions that fcc polymorphous modifications of Ce and La make up the continuous sequence of solid solutions. In addition, a small deviation from Vegard's law is observed.

La–Ni system

Phase equilibrium in the lanthanum alloys with nickel in the range from 0 to 100 at.% Ni has been studied in Refs. [12,15–18]. Two variants of the total constitution diagram for the La–Ni system are given in Figs. 2 and 3.

The La_3Ni, LaNi, $LaNi_2$, $LaNi_3$–$LaNi_4$ and $LaNi_5$ compounds are formed according to the La–Ni constitution diagram described in the handbook [12]. The construction of the La–Ni constitution diagram in the concentration range between 50 and 83.3 at.% Ni was refined in the paper [17].

The six compounds as LaNi, $LaNi_{1.51}$, $LaNi_{2.286}$, $LaNi_3$, La_2Ni_7 and $LaNi_5$ were found in the investigated concentration range. The $LaNi_2$ compound reported in Refs. [12,16] does not exist in equilibrium conditions, it is a metastable phase.

Fig. 2 demonstrates the La–Ni constitution diagram [15–17] in the concentration range from 50 to 83.3 at.% Ni. The part of the constitution diagram above 1100 °C and at the nickel content from 83 to 100 at.% is given according to the evidence derived from Refs. [18], and at the nickel content from 0 to 45 at.% according to [12].

La_3Ni, LaNi and $LaNi_5$ compounds are melted congruently at 532, 715 and 1350 °C [18]. La_2Ni_3, La_7Ni_{16}, $LaNi_3$ and La_2Ni_7 compounds are formed by peritectic reactions at 688, 714, 811 and 1014 °C, respectively. The La_2Ni_7 compound undergoes a polymorphous transformation at ~976 °C: $\beta La_2Ni_7 \rightleftarrows \alpha La_2Ni_7$. Four eutectics crystallize in the system:

$$(\beta\,La) + La_3Ni \text{ at } \sim 527\,^{\circ}C \text{ and } \sim 17 \text{ at.\% Ni;}$$

$$La_7Ni_3 + LaNi \text{ at } 517\,^{\circ}C \text{ and } \sim 31 \text{ at.\% Ni;}$$

$$LaNi + La_2Ni_3 \text{ at } 675 \pm 5\,^{\circ}C \text{ and } 57,7 \text{ at.\% Ni;}$$

$$LaNi_5 + (Ni) \text{ at } 1270\,^{\circ}C \text{ and } 93 \text{ at.\% Ni.}$$

La solubility in Ni was investigated in Ref. [19] and it was found to be 0.346 mass.% at 1050 °C, 0.309 mass.% at 1020 °C and 0.380 mass.% at 950 °C.

Ce–Ni system

Fig. 4 demonstrates the Ce–Ni constitution diagram reported in a number of papers [20–27] which summarize the results of DTA, X-ray, metallographic studies on the alloys prepared using 98–99% pure Ce (by mass).

There exist six compounds in the system. Ce_7Ni_3, CeNi and $CeNi_5$ melt congruently at 477, 495, 1210 °C, respectively. The rest of the compounds are formed by peritectic reactions. The nonvariant reactions proceeding in the Ce–Ni system are given in Table 1.

The reciprocal solubility of components is negligible. The Ce solubility in Ni was found to be 0.05 and 0.04 at.% at the temperatures of 1200 and 400 °C, respectively [28].

Ce–La–Ni system

The present study of the Ce–La–Ni system has been undertaken to check the evaluated literature data and aimed at refining the position of phase boundaries in the nickel corner of the Ce–La–Ni system at melting points (crystallization of alloys). Several experimental alloys have been produced at 1–5 at.% intervals in the region rich in nickel.

The alloys have been smelted in an electric arc furnace with a permanent tungsten electrode on the copper water-

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