

INFLUENCE OF Ni AND La ADDITIONS UPON PECULIARITIES OF HYDROGENATION AND HYDROGEN CAPACITY OF COMPOSITES BASED ON Zr-CONTAINING ALLOYS

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Nickel-metal-hydride (Ni-MH) accumulators attract significant attention due to their high service characteristics and ecological safety. Materials for negative electrodes of Ni-MH accumulators are rare-earth-containing alloys of the AB₅-type, Zr-based alloys, TiFe, magnesium and its alloys.

Prospective materials for such a case are Zr-based alloys of the AB₂-type (Laves phases), possessing some advantages as compared with other materials: capacity of Zr-containing alloys is higher by 30% than that of rare-earth-containing alloys of the AB₅-type. In many cases the AB₂-type alloys are hydridized more easily as compared with TiFe and LaNi₅, because of the existence of a very thin surface layer in Zr-based alloys (e.g., the oxide layer on the surface of ZrMn₂ reaches 50–75 Å, whereas this layer on the surface of LaNi₅ reaches 200 Å). Additionally, Zr-based alloys are better cycling in comparison with magnesium-based alloys.

Among main disadvantages of Zr-containing alloys preventing their wide utilization, one should mention the necessity of additional both treatment and activation of alloys, which are covered by a thin layer of oxides and hydroxides. During electrochemical hydrogenation, activation is complicated by a passion influence of electrolyte with respect to the surface of a hydrogenating electrode. In such a case, a small addition of Ni powder as an activator of hydrogen chemisorption in a hydriding reaction, can influence positively electrochemical hydrogenation. A benefit upon this process can be achieved by addition of an easily hydriding rare-earth-containing alloy, which plays a role of “hydrogen pump” and favors to carry hydrogen inside an electrode increasing a degree of hydrogenation. Therefore, it is of great importance to study systematically peculiarities of electrochemical hydrogenation of composite electrodes based on alloys of the AB₂-type with hydriding rare-earth-containing additions. For additional activation of Zr-containing alloys, in the present work the method of mechanical influence upon the electrode material for achieving its optimal state for hydriding was used.

The objects of the present study are composite electrodes made from mixtures of powders of Zr-based AB₂-type alloys and a rare-earth-containing AB₅-type intermetallic with different time of milling in a GM 9458 vibrator (Germany). Electrochemical studies of the samples were carried out at 25 °C in a glass three-electrode cell, with separated cathode and anode space, using a PI-50-1.1 potentiometer. Hydrogen capacity of electrodes was determined in non-equilibrium conditions: at the first stage of the experiments, we determined capacity at high discharge currents; at the second stage, the current value was decreased by about 10 times. The full electrode capacity was determined by summation of the two above mentioned capacities.

An optimum concentration of Ni and La addition, which allows reaching maximum hydrogen content in the sample within the time prescribed, has been determined. A special specimen microstructure has been elaborated. This microstructure ensures an optimum value of section surface for composite/catalyst allowing maximum hydrogen capacity.

Two samples were chosen for our studies, which differ from each other only by substitution aluminum for vanadium. For a multicomponent Zr-based alloy containing aluminum (0.1 wt.%), additions of 10%, 20% and 50% of nickel (relative to the total electrode weight) with 15 min and 1 h milling time, the maximum hydrogen capacity corresponds to an electrode containing 10 wt.% Ni after its 1 h milling. This multicomponent Zr-containing alloy, at the very beginning of its hydrogenation, forms a hydride around catalyst particles. The less catalyst content, the smaller hydride film is formed on the alloy surface favoring inserting hydrogen into a sample volume. The Zr-based alloy containing vanadium reveals the highest hydrogen capacity when adding 50% Ni and after 1 h milling.

Due to the fact that with increasing catalyst content in an alloy its hydrogen content (wt.%) decreases, the base alloys for the present study regarding the influence of addition of lanthanum upon Zr-containing composite hydrogen capacity, we have chosen Zr-based alloys with

aluminum and 10% Ni. The alloys differ from each other by substitution of chromium for cobalt and mischmetal. We have studied the influence of addition of easy-hydriding a lanthanum-containing intermetallic in the quantity 10%, 15%, 20% and 30% wt.

Data regarding the influence of addition of lanthanum upon electrochemical characteristics and hydrogen capacity of the composites (as a factor of component content in the initial Zr-based alloy) have been obtained. Due to our results, the multicomponent Cr-containing alloy possesses the highest hydrogen capacity when adding 15% wt. of the La-containing intermetallic. Addition of 10% and 20% of the intermetallic does not influence the

composite hydrogen capacity. However, the addition of 15% of the intermetallic increases the hydrogen capacity by 25% (in comparison with that of the base alloy) even in the first cycles of hydrogenation. The multicomponent Zr-based alloy containing cobalt and mischmetal possesses the highest hydrogen capacity when adding 20% of the La-containing intermetallic. The alloy reveals very reproducible parameters during its hydriding-dehydriding.

The X-ray photoelectron spectroscopy method has been employed in the present work to study the influence of the additions upon the chemical state of a surface of the Zr-containing alloys after their mechanochemical milling.