A USE OF INTERMETALIC COMPOUNDS OF $MmNi_{5-x-y-z}Co_xAl_yMn_z$ TYPE IN PHOTOELECTROCHEMICAL AND ELECTROCHEMICAL SYSTEMS AS HYDROGEN ACCUMULATORS

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Introduction

Alloys on the base of $LaNi_5$ are extensively used for the manufacture of cathodes of metal hydride cells. The optimal cobalt content in these alloys required for providing long cycle life is about 30 mass %. It is known that the partial substitution of La in a $LaNi_5$-base alloy by a mish metal enables one to reduce substantially the Co content (to 10 mass %) in them and, hence, to decrease significantly the cost of the alloy. However, such substitution often leads to the deterioration of a number of technological characteristics of the alloys, specifically, to an increase in the equilibrium hydrogen pressure in the hydride. The partial substitution of Ni by Al, Mn, and Cr in the alloys makes it possible to decrease the negative effect caused by the introduction of a mish metal. Ukraine has its own resources of rare-earth metals, including a mish metal containing 20–25% La, 10–15% (Pr+Nd), 48–55% Ce, 0.5–1.0% Dy, and 1.0–1.5% Sm. The aim of the present work is to investigate the possibility of providing high sorption and electrochemical characteristics of alloys with the indicated lanthanum content in a mish metal.

Results and discussion

A complex investigation of alloys of two compositions $MmNi_{4.3}Mn_{0.5}Al_{0.2}$ and $MmNi_{3.5}Co_{0.7}Al_{0.8}$ was performed. The alloys were obtained by a powder metallurgy method, namely by gas-atomizing a metal in an inert atmosphere (GA).

An X-ray phase analysis of powders of the alloys showed the presence of only diffraction reflexes characteristic of hexagonal $LaNi_5$ (the space group P6/mmm, the structural type $CaCu_5$), which indicates that the alloys are mono phase. The substitution of La by the mish metal leads to a substantial decrease in the lattice constant *a* and, as a result, an increase in the volume of the unit cell (V_{cell}), which is observed for La-containing alloys upon adding aluminum, does not occur (table 1) [1].

The integral enthalpy of dehydrogenation of the $MmNi_{3.5}Co_{0.7}Al_{0.8}$ alloy was determined by the calorimetric method (an NT-s-400 calorimeter). It was established that the general view of the thermogram of hydrogen desorption from the $MmNi_{3.5}Co_{0.7}Al_{0.8}$ alloy resembles the general view of desorption thermograms obtained for alloys with a high cobalt content [2]. The initial temperature of hydrogen desorption is higher by almost 100ºC than that for $LaNi_5H_x$, and on the thermogram of the $MmNi_{3.5}Co_{0.7}Al_{0.8}H_x$ alloy, an additional maximum appears in the temperature range characteristic of cobalt-substituted alloys. The dehydrogenation enthalpy ($\Delta H_{deg.}$) of the $MmNi_{3.5}Co_{0.7}Al_{0.8}$ alloy which was calculated for the thermograms, is equal to 47.2 kJ/mole H_2, which is higher by almost 30% than that for $LaNi_5H_x$.However, the value of $\Delta H_{deg.}$ is much higher than that for Co-substituted alloys (to 2.5 cobalt atoms) and close to the values of ΔH characteristic of $LaNi_{5-x}M_x$ ternary alloys [1].

Table 1.

Сплав	*a*, Å	$V_{cell.}$, Å^3	$\Delta H_{deg.}$, kJ/mol H_2
$LaNi_5$	5,0174	86,93	32,6
$LaNi_{4,0}Al_{1,0}$	5,0478	90,00	52,3
$LaNi_{4,0}Co_{1,0}$	5,0267	87,23	35,7
$MmNi_{3.5}Co_{0.7}Al_{0.8}$	4,9780	87,34	47,2
$MmNi_{4.3}Al_{0.2}Mn_{0.5}$	4,9620	86,30	-

An investigation of the electrochemical characteristics of the $MmNi_{3.5}Co_{0.7}Al_{0.8}$ and $MmNi_{4.3}Mn_{0.5}Al_{0.2}$ alloys showed (Table 2) that the equilibrium potentials of formation ($E_{M/MH}$) and decomposition ($E_{MH/M}$) of hydrides practically coincide, and, for both alloys, these values are more positive (by 20–40 mV) than those for $LaNi_5$ and its Co-containing alloys. That is, on adding simultaneously a mish metal and Al in an AB_5 alloy, aluminum, as in ternary alloys, favors the formation of more stable hydride, i.e., for the alloy, a correlation between the quantities $E_{M/MH}$ and ΔH is observed.

The quantities $E_{M/MH}$ and $E_{MH/M}$ of the $MmNi_{4.3}Mn_{0.5}Al_{0.2}$ alloy are more negative (by 20–30 mV) than those for the

$MmNi_{3.5}Co_{0.7}Al_{0.8}$ alloy. The cathodic displacement of the value of $E_{M/MH}$ (i.e., an increase of the equilibrium hydrogen pressure in hydride) is most probably connected with a smaller influence of manganese on this characteristic and with the low aluminum content in the alloy.

An investigation of the kinetic characteristics of the cathodic process showed that the activation of the surface of the alloy with a large aluminum content is less efficient than that for the Mn-containing alloy, which is evidenced by the difference in the values of the exchange current (i_o) on the initial surface (Table 2). However, in the subsequent charge/discharge cycles, the rate of the reaction of exchange with hydrogen, particularly for the $MmNi_{3.5}Co_{0.7}Al_{0.8}$ alloy, increases (Table 2). At E = –0.95 V, which corresponds to the potential of the optimal power output in a photoelectrochemical (PEC) cell [1] and is close the value of $E_{MH/M}$ of the alloys, and the cathodic currents further increase. That is the charge of cathodes in the PEC cell can be realized by large currents (tens of milliamperes).

Table 2. Electrochemical, kinetic and sorption characteristics of alloys of $MmNi_{5-x-y-z}Co_xAl_yMn_z$ type.

Alloy	№ cycle	$E_{M/MH}$/ $E_{MH/M}$, V	i_0, mA	$I_{0.95B}$, mA	Cdisch. mA×h/g
1*	init	-0,90/ -0,89	-0,2	-19,0	-
	1		-	-	320
	2		-8,4	-25,0	350
	3		-11,0	-29,0	380
2**	Init.	-0,93/ -0,91	-3,2	-14,0	-
	1		-3,2	-22,0	320
	2		-6,0	-44,0	360

1* - alloy $MmNi_{3.5}Co_{0.7}Al_{0.8}$
2** - alloy $MmNi_{4..3}Mn_{0..5}Al_{0.2}$.

An analysis of the kinetic curves constructed in the E – lg$i$ coordinates showed that, for both alloys, the slope of the linear region at potentials $-0.89 \le E \le -1$ V is close to 0.12 V, which agrees well with the theoretical Tafel slope (2RT/F) and with the assumption that the reaction $H_2O + e^- \rightarrow H_{(a)} + OH^-$ is a rate-determining reaction.

Electrodes of both alloys $MmNi_{4.3}Mn_{0.5}Al_{0.2}$ and $MmNi_{3.5}Co_{0.7}Al_{0.8}$ showed a high sorption capacity in the first three charge/discharge cycles (320–380 mA×h/g).

The cyclic charge–discharge characteristics of the $MmNi_{4.3}Mn_{0.5}Al_{0.2}$ alloy were investigated using a 70-channel unit, in which the process and analysis of results was performed with a computer. A closed cell with a diameter of 11.6 mm and a thickness of 4.2 mm, in which, besides a working electrode, there were a $Ni(OH)_2$ counter electrode and a 6M KOH electrolyte, was used. The weight of the alloy in the investigated electrodes was 0.1 g and the charge-discharge current was 6.5 mA. Before testing the surface of the electrodes was chemically activated. The results of the electrochemical tests of the gas-atomized $MmNi_{4.3}Mn_{0.5}Al_{0.2}$ alloy showed that, even in the first cycle, the electrochemical capacity is 310 mA×h/g and ranges from 317 to 323 mA×h/g in 10 subsequent cycles.

Conclusions

1. The influences of the substitution of La by a mish metal and of the complex alloying of two alloys $MmNi_{3.5}Co_{0.7}Al_{0.8}$ and $MmNi_{4..3}Mn_{0..5}Al_{0.2}$ obtained by a powder metallurgy method on their structure, thermodynamic, electrochemical, and sorption characteristics were investigated.

2. It was established that the addition of aluminum in the alloys made it possible to decrease the negative influence of the mish metal on the equilibrium potential of formation of hydride; the alloys are readily activated, have good kinetic and sorption characteristics, and a long cycle life.

3. The complex of the obtained characteristics enables us to recommend the investigated alloys as cathode materials for Ni–MH and PEC current sources.

References

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