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Investigation of the influence of nickel content on the correlation between the hydrogen equilibrium pressure for hydrogen absorbing alloys and the capacity of MH electrodes in open and closed cells

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Abstract Two series of overstoichiometric AB_{2.4} alloys [(Zr_{0.35}Ti_{0.65})(V_{1.33}Cr_{0.4}Fe_{0.27})_{2-x}Ni_{0.4+x} and (Zr_{0.5}Ti_{0.5})(V_{0.8}Mn_{0.8}Cr_{0.4})_{2-x}Ni_{0.4+x}], differing in the Zr to Ti ratios in group A and the presence of Mn or Fe in group B, were examined to consider the influence of various amounts of nickel on the structural parameters following the sorption of hydrogen. To predict the electrochemical behaviour of the prepared alloys as negative electrodes for Ni-MH cells, the pressure-composition isotherms (PCT) determined for the gas/solid phase system were correlated with the electrochemical pressure-composition (EPC) isotherms estimated from the rest potential of the alloy electrode. For preliminary assessment of the practical usefulness of the prepared samples, the electrodes made of all the alloys were subjected to charge/discharge measurements in a half-cell in 6 M KOH solution and the discharge capacities were estimated. Of the alloys with Fe and Mn components, the samples (Zr_{0.35}Ti_{0.65})(V_{0.93}Cr_{0.28}Fe_{0.19}Ni_{1.0}) and (Zr_{0.5}Ti_{0.5})(V_{0.68}Mn_{0.68}Cr_{0.34}Ni_{0.7}) provided the highest capacities. These alloys were chosen for testing the charge/discharge cycleability in closed Ni-MH cells. The reversibility of the cell with the former sample decreased significantly around the 25th cycle, whereas the discharge capacity of the cell with the latter sample remained almost unchanged during 100 cycles of testing.

Keywords Hydrogen storage alloys · Hydrogen absorption · Nickel-metal hydride battery · Electrochemical properties

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Introduction

Over many years the Central Laboratory of Batteries and Cells in Poland has been conducting systematic investigations on hydrogen absorbing alloys of the AB₂ type. At present, overstoichiometric alloys of the AB_{2.4} type are being examined. Multicomponent alloys belonging to the Laves phase of the AB_{2.4} type offer great possibilities for changing their chemical composition and thereby physicochemical properties. The suitability of an alloy for an electrode material is closely connected with the nickel content acting as a catalyst in an electrode reaction.

Systematic modification of the alloy composition was carried out previously to change the mutual proportions of the components in group A [1, 2]. In the present paper we attempted the optimization of the nickel proportion in relation to other elements comprising group B for the chosen overstoichiometric alloys of the AB_{2.4} type.

Experimental

To approach to the optimum composition of the hydride electrode, designed to cooperate with a highly efficient positive electrode in alkaline media, the physicochemical and electrochemical properties of the alloy electrodes were subjected to experimental testing.

Two different groups of alloys of general formulas (a) (Zr_{0.35}Ti_{0.65})(V_{1.33}Cr_{0.4}Fe_{0.27})_{2-x}Ni_{0.4+x} ($x=0, 0.3, 0.5, 0.6, 0.7, 0.73, 0.75, 0.8, 0.9, 1.2$) and (b) (Zr_{0.5}Ti_{0.5})(V_{0.8}Mn_{0.8}Cr_{0.4})_{2-x}Ni_{0.4+x} ($x=0, 0.2, 0.3, 0.4, 0.6, 0.9$) were examined separately. Multicomponent alloys of the above formulas were prepared in an arc furnace in an argon atmosphere using ferrovanadium (80.6% V, 18.7% Fe-Baildon) as the vanadium source (alloys a) and the mixture of pure metals (99.9% Merck; alloys b) in proper atomic proportions [1, 2]. The casting was carried out in a Bühler arc furnace using a water-cooled copper crucible. The electrode material was produced by mechanical grinding in a hydraulic press followed by crushing to a fine powder via cyclic hydrogen absorption/desorption from the gaseous phase. Electrodes of hydrogen reversibly absorbing alloys were prepared by mixing the alloy powder (0.04–0.08 mm grain size) with 10 wt.% addition of tetracarboxylnickel. This powder mixture was pressed at 80 kN/cm² into 10.4×1.4 mm tablets. A tablet was then placed in a small basket made of nickel gauze (current collector) and pressed again

using a hand press. Before electrochemical testing the working electrodes were chemically preactivated by boiling in 12 M KOH solution. After activation they were put in an electrolytic cell filled with 6 M KOH. A Hg/HgO/6 M KOH electrode was used as the reference electrode. The $(\text{Ni}(\text{OH})_2/\text{NiOOH})$ electrode, made on a sintered nickel carrier, served as the auxiliary electrode, the capacity of which many times exceeded that of the working electrode. The constant current charge/discharge measurements were performed at current density of $i=40$ mA/g. During the first cycle the charge process was conducted until the beginning of hydrogen evolution on the electrode. After 1 h of a rest period for potential equilibration the electrode was discharged to a potential of -0.7 V. In the subsequent cycles the electrode was charged up to 160% of the electrode capacity in relation to the discharge capacity of the first cycle. The cyclic behaviour of the alloy anodes was examined in a closed HB 116/054 cell (according to the International Standard IEC no. 61808, related to the hydride button rechargeable single cell).

Results and discussion

Characteristics of the $(\text{Zr}_{0.35}\text{Ti}_{0.65})(\text{V}_{1.33}\text{Cr}_{0.4}\text{Fe}_{0.27})_{2-x}\text{Ni}_{0.4+x}$ alloys

Based on the $(\text{Zr}_{0.35}\text{Ti}_{0.65})(\text{V}_{0.85}\text{Cr}_{0.26}\text{Fe}_{0.17}\text{Ni}_{1.13})$ alloy which has been reported in a previous paper [1], the nickel content is here changed in relation to the remaining components of group B. The chemical and XRD phase compositions and the unit cell volumes in the multicomponent alloys are listed in Table 1. The capacity values of these alloys, estimated in half-cells (so-called open cells), are shown in Fig. 1. Three alloys demonstrating the highest capacities were selected from this group and subjected to detailed investigations. The chemical compositions of these alloys are given in Table 2.

In the next stage of the investigations, the effect of the modified composition of the alloys on their capacity and on the hydrogen absorption/desorption equilibrium pressure was examined. The analysis of hydrogen absorption/desorption isotherms for the gas/solid system (pressure-composition isotherms, PCT) [3, 4] is one of the criteria for the estimation of a hydrogen absorbing alloy as an anode material for Ni-MH cells. Alloys absorbing large amounts of hydrogen at very low pressures (below 0.1 kPa) are useless as an electrode material

owing to the excessively high value of the hydrogen bond energy in the alloy, which causes the electrode reaction to be irreversible. Alloys for which the absorption plateau equilibrium pressure surpasses that in a closed cell (100 kPa) were recognized as unserviceable owing to their low value of the hydrogen bond energy [5, 6]. Alloys absorbing large amounts of hydrogen in the pressure range from 0.1 to 100 kPa are considered as suitable materials for MH electrodes.

For the alloys described in Table 2, PCT absorption/desorption isotherms for hydrogen were determined by the Sievert method [3]. Prior to measuring the isotherms, sample pretreatment was carried out by heating the alloy in a vacuum reactor at 680 K for 4 h to remove all volatile impurities. The measurements of the hydrogen desorption isotherms were carried out after cooling the system to room temperature. The hydrogen content in the sample was calculated volumetrically, based on the initial and final values of the pressure for the given volumes of reactor and supplied hydrogen. The hydrogen desorption isotherms determined in the solid/gas system for alloys II C, II Ca and II Cb are presented in Fig. 2.

On examining these isotherms one can observe that these alloys differ from each other. Differences in the amounts of hydrogen absorbed by the alloys are noticeable for an equilibrium pressure lower than 0.1 MPa. For the given pressure (e.g., between 0.1 and 0.05 MPa) the concentration of hydrogen changes according to the following order: II C > II Ca > II Cb.

Electrochemical hydrogen absorption/desorption isotherms (electrochemical pressure-composition isotherms, EPC) were measured for the above alloys. The equilibrium pressure of hydrogen, $p(\text{H}_2)$, in the hydride electrode, determined during the charge/discharge cycling, is the parameter allowing us to predict the practical usefulness of an alloy as the negative electrode in Ni-MH cells.

EPC isotherms were recorded in the course of the periodic (0.5 h) charge/discharge cycles at a current density $i=40$ mA/g of the alloy. After each cycle the electrodes were subjected to relaxation (0.5 h) at open circuit and then the measurements were continued. The relation between the hydrogen equilibrium pressure and

Table 1. Chemical and phase compositions and unit cell volumes for alloys of general formula $(\text{Zr}_{0.35}\text{Ti}_{0.65})(\text{V}_{1.33}\text{Cr}_{0.4}\text{Fe}_{0.27})_{2-x}\text{Ni}_{0.4+x}$

Symbol of alloy	Chemical composition	Phase composition ^a	Unit cell volume (nm ³)
II	$(\text{Zr}_{0.35}\text{Ti}_{0.65})(\text{V}_{0.85}\text{Cr}_{0.26}\text{Fe}_{0.17}\text{Ni}_{1.13})$	H ^b	0.1667
II A	$(\text{Zr}_{0.35}\text{Ti}_{0.65})(\text{V}_{1.33}\text{Cr}_{0.41}\text{Fe}_{0.27}\text{Ni}_{0.4})$	H ^b	0.1773
II B	$(\text{Zr}_{0.35}\text{Ti}_{0.65})(\text{V}_{1.13}\text{Cr}_{0.35}\text{Fe}_{0.23}\text{Ni}_{0.7})$	H	0.1702
II Ca	$(\text{Zr}_{0.35}\text{Ti}_{0.65})(\text{V}_{1.0}\text{Cr}_{0.30}\text{Fe}_{0.20}\text{Ni}_{0.9})$	H	0.1668
II C	$(\text{Zr}_{0.35}\text{Ti}_{0.65})(\text{V}_{0.93}\text{Cr}_{0.28}\text{Fe}_{0.19}\text{Ni}_{1.0})$	H ^c	0.1693
II Cb	$(\text{Zr}_{0.35}\text{Ti}_{0.65})(\text{V}_{0.86}\text{Cr}_{0.26}\text{Fe}_{0.18}\text{Ni}_{1.1})$	H	0.1666
II D	$(\text{Zr}_{0.35}\text{Ti}_{0.65})(\text{V}_{0.73}\text{Cr}_{0.22}\text{Fe}_{0.15}\text{Ni}_{1.3})$	H ^c	0.1664
II E	$(\text{Zr}_{0.35}\text{Ti}_{0.65})(\text{V}_{0.53}\text{Cr}_{0.16}\text{Fe}_{0.11}\text{Ni}_{1.6})$	H ^c	0.1627
II F	$(\text{Zr}_{0.35}\text{Ti}_{0.65})(\text{V}_{0.83}\text{Cr}_{0.25}\text{Fe}_{0.17}\text{Ni}_{1.15})$	H ^c	0.1675
II G	$(\text{Zr}_{0.35}\text{Ti}_{0.65})(\text{V}_{0.8}\text{Cr}_{0.24}\text{Fe}_{0.16}\text{Ni}_{1.2})$	H ^c	0.1674

^aH = Hexagonal Laves phase of the MgZn_2 type

^bTraces of unidentified phases with reflections corresponding to $d=0.316$ and 0.281 nm

^cTraces of unidentified phases with reflections corresponding to $d=0.316$, 0.284 and 0.261 nm

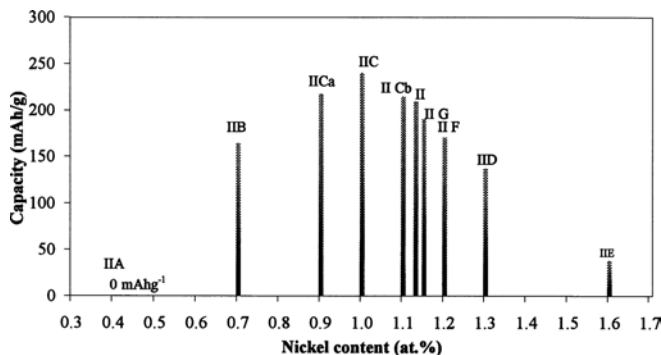


Fig. 1. The influence of nickel content on the discharge capacity of $(Zr_{0.35}Ti_{0.65})(V_{1.33}Cr_{0.40}Fe_{0.27})_{2-x}Ni_{0.4+x}$ at 293 K

Table 2. Chemical compositions and discharge capacities for hydrogen absorbing alloys of general formula $(Zr_{0.35}Ti_{0.65})(V_{1.33}Cr_{0.40}Fe_{0.27})_{2-x}Ni_{0.4+x}$

Symbol of alloy	Chemical composition	Discharge capacity (mAh/g alloy)
II Ca	$(Zr_{0.35}Ti_{0.65})(V_{1.0}Cr_{0.30}Fe_{0.20}Ni_{0.9})$	218
II C	$(Zr_{0.35}Ti_{0.65})(V_{0.93}Cr_{0.28}Fe_{0.19}Ni_{1.0})$	240
II Cb	$(Zr_{0.35}Ti_{0.65})(V_{0.86}Cr_{0.26}Fe_{0.18}Ni_{1.1})$	215

the amount of hydrogen absorbed in the alloy electrodes was determined on the basis of the Nernst equation, which takes into account the coefficient of hydrogen volatility:

$$E_s = -0.9325 - 0.0291 \log p(H_2)/p_0 \quad (1)$$

where E_s is the rest potential of the (MH) electrode vs. the Hg/HgO/6 M KOH reference electrode, $p(H_2)$ is the equilibrium pressure, and p_0 is the standard pressure.

In the present paper the capacity of the alloy electrode in relation to the amount of absorbed hydrogen (wt.%) was calculated based on the input/output charge. In accordance with the above equation, the change of one order of magnitude in hydrogen pressure in the alloy results in a change in the electrode potential of 29 mV. It is well known that alloys exhibiting a lack of a well-formed part of a small rise of pressure on their absorption/desorption isotherms can be recognized as useful materials for negative electrodes in Ni-MH cells. Electrochemical hydrogen absorption/desorption isotherms determined for alloys II C, II Ca and II Cb of general formula $(Zr_{0.35}Ti_{0.65})(V_{1.33}Cr_{0.40}Fe_{0.27})_{2-x}Ni_{0.4+x}$ are shown in Fig. 3. From comparison of the EPC curves for desorption, one can see that alloys II C and II Ca demonstrate significantly higher concentrations of hydrogen in practically preferred equilibrium pressure (< 0.05 MPa) as compared to alloy II Cb. This means that the former alloys offer good properties for application as negative electrodes. Alloy II Cb requires a distinctly higher pressure for sorption of hydrogen. Moreover, on EPC absorption/desorption curves for sample II Cb, a wide hysteresis appears which indicates

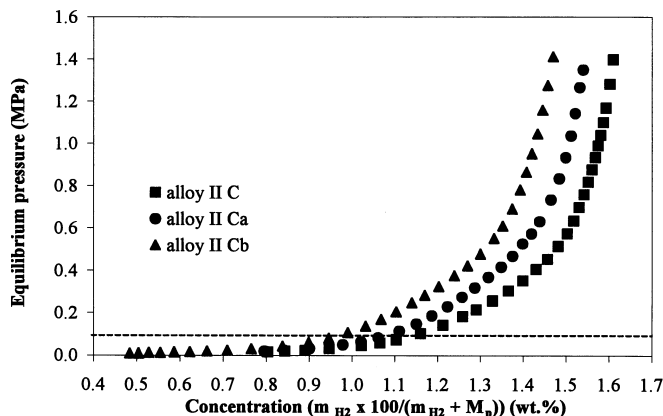


Fig. 2. Pressure-composition isotherms for desorption of hydrogen from the gas phase using $(Zr_{0.35}Ti_{0.65})(V_{1.33}Cr_{0.40}Fe_{0.27})_{2-x}Ni_{0.4+x}$ at 293 K (m_{H_2} = mass of absorbed hydrogen, M_p = mass of sample)

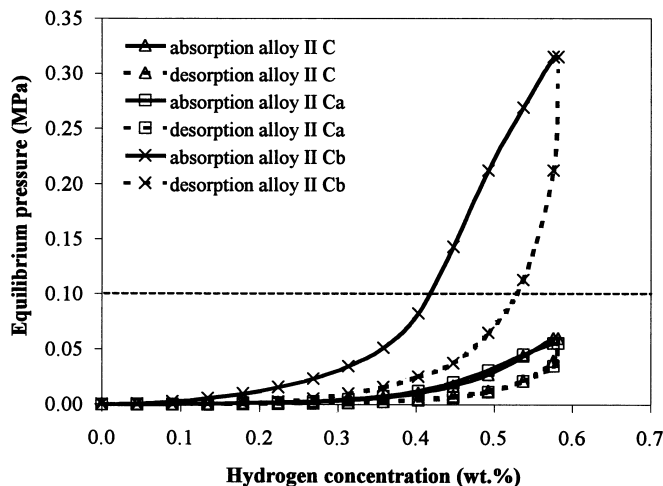


Fig. 3. Electrochemical pressure-composition isotherms for absorption/desorption of hydrogen using $(Zr_{0.35}Ti_{0.65})(V_{1.33}Cr_{0.40}Fe_{0.27})_{2-x}Ni_{0.4+x}$ at 293 K

that only part of the hydrogen can be recovered during the discharged run of the Ni-MH cell. It is worth noting that the conclusions arising from analysis of the EPC curves (Fig. 3) are in good agreement with those resulting from the PCT curves presented in Fig. 2.

Based on these conclusions, button cells (so-called closed cells) were made using alloy II C of formula $(Zr_{0.35}Ti_{0.65})(V_{0.93}Cr_{0.28}Fe_{0.19}Ni_{1.0})$. The cells were subjected to the cyclic charge/discharge life tests. The changes in discharge capacity upon cycling are depicted in Fig. 4. Owing to a steep drop in capacity, only the first 40 cycles are shown in this figure.

Characteristics of the $(Zr_{0.5}Ti_{0.5})(V_{0.8}Mn_{0.8}Cr_{0.4})_{2-x}Ni_{0.4+x}$ alloys

In earlier unpublished work devoted to another group of alloys, the compound with formula $(Zr_{0.5}Ti_{0.5})$

($V_{0.8}Mn_{0.8}Cr_{0.4}$) was examined. The preliminary data showed that this nickel-free alloy is electrochemically inactive owing to a low ability to absorb hydrogen (see alloy I in Fig. 5). Surprisingly, PCT absorption/desorption isotherms for hydrogen for this alloy exhibited very large amounts of absorbed hydrogen and good reversibility of the desorption/absorption process (Fig. 5). On the assumption that the presence of nickel in group B can improve its electrochemical properties, the purpose of our work was to add various amounts of nickel to the ($Zr_{0.5}Ti_{0.5}$)($V_{0.8}Mn_{0.8}Cr_{0.4}$) alloy. The composition of group B was changed in such a way to find the optimum content of nickel in relation to the remaining elements of this group. The chemical and phase compositions and the unit cell volumes of the original ($Zr_{0.5}Ti_{0.5}$)($V_{0.8}Mn_{0.8}Cr_{0.4}$) alloy and the nickel-modified ($Zr_{0.5}Ti_{0.5}$)($V_{0.8}Mn_{0.8}Cr_{0.4}$) $_{2-x}Ni_{0.4+x}$ alloys are listed in Table 3. Discharge capacities for all the investigated alloys, estimated in a half-cell (so-called open cell), are depicted in Fig. 6.

Three alloys representing the highest capacities (denoted I B, I Ba and I Bb) were selected for further examination. The chemical compositions and discharge capacities for these alloys are given in Table 4, whereas PCT absorption/desorption isotherms for hydrogen and ECT isotherms for hydrogen desorption are presented in Figs. 7 and 8, respectively.

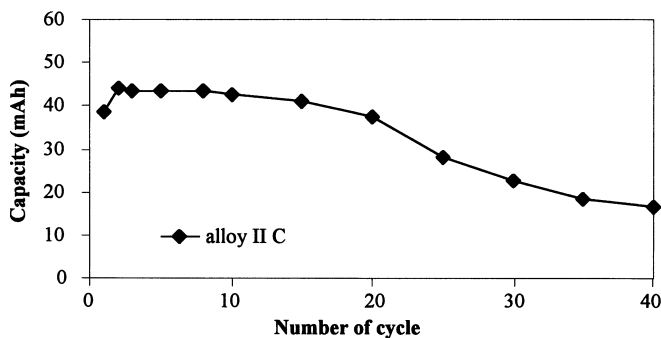


Fig. 4. Durability of the button cell with a negative electrode made of alloy II C, ($Zr_{0.35}Ti_{0.65}$)($V_{0.93}Cr_{0.28}Fe_{0.19}Ni_{1.0}$)

Table 3. Chemical and phase compositions and unit cell volumes for alloys of general formula ($Zr_{0.5}Ti_{0.5}$)($V_{0.8}Mn_{0.8}Cr_{0.4}$) $_{2-x}Ni_{0.4+x}$

Symbol of alloy	Chemical composition	Phase composition ^a	Unit cell volume (nm ³)
I	($Zr_{0.5}Ti_{0.5}$)($V_{0.8}Mn_{0.8}Cr_{0.4}$)	H ^b	0.1796
I A	($Zr_{0.5}Ti_{0.5}$)($V_{0.8}Mn_{0.8}Cr_{0.4}Ni_{0.4}$)	H	0.1739
I Ba	($Zr_{0.5}Ti_{0.5}$)($V_{0.72}Mn_{0.72}Cr_{0.36}Ni_{0.6}$)	H ^c	0.1709
I B	($Zr_{0.5}Ti_{0.5}$)($V_{0.68}Mn_{0.68}Cr_{0.34}Ni_{0.7}$)	H	0.1705
I Bb	($Zr_{0.5}Ti_{0.5}$)($V_{0.64}Mn_{0.64}Cr_{0.32}Ni_{0.8}$)	H ^c	0.1713
I C	($Zr_{0.5}Ti_{0.5}$)($V_{0.56}Mn_{0.56}Cr_{0.28}Ni_{1.0}$)	H	0.1688
I D	($Zr_{0.5}Ti_{0.5}$)($V_{0.44}Mn_{0.44}Cr_{0.22}Ni_{1.3}$)	H ^d	0.1660

^aHexagonal Laves phase of the MgZn₂ type

^bTraces of unidentified phase with reflections $d=0.333$ and 0.296 nm

^cTraces of unidentified phase with reflections $d=0.314$ nm

^dTraces of unidentified phase with reflections $d=0.314$ and 0.293 nm

As can be seen from Fig. 7, the pressure curves recorded for all three alloys during desorption of hydrogen are relatively flat for an equilibrium pressure lower than 0.1 MPa. On the other hand, distinct differences are noticeable between these alloys on comparing their electrochemical hydrogen absorption/desorption isotherms (Fig. 8). All the isotherms lie in the pressure range satisfying a condition for their practical use in Ni-MH cells. It can be seen from this figure that alloy I B absorbs much more hydrogen than alloys I Ba and I Bb.

ECT curves corresponding to alloys I Ba and I Bb (Fig. 8) could be recorded only up to the equilibrium pressures of 0.0065 MPa and 0.0214 MPa, respectively, owing to the evolution of hydrogen occurring at higher pressures. Based on these results, alloy I B of formula ($Zr_{0.5}Ti_{0.5}$)($V_{0.68}Mn_{0.68}Cr_{0.34}Ni_{0.7}$) was assumed to be the best candidate for electrochemical application. Indeed, this alloy exhibited the highest discharge capacity (225 mAh/g alloy) when tested in a half-cell (Table 4, Fig. 6). For the above reasons, alloy I B was then subjected to the cyclic life tests in the button cell (so-called closed cell). Because no rapid decrease in discharge capacity was observed for a long time (Fig. 9), the measurements were stopped after 100 cycles. In recent work (unpublished) attempting the elucidation of the worsening of the charge/discharge reversibility of the button

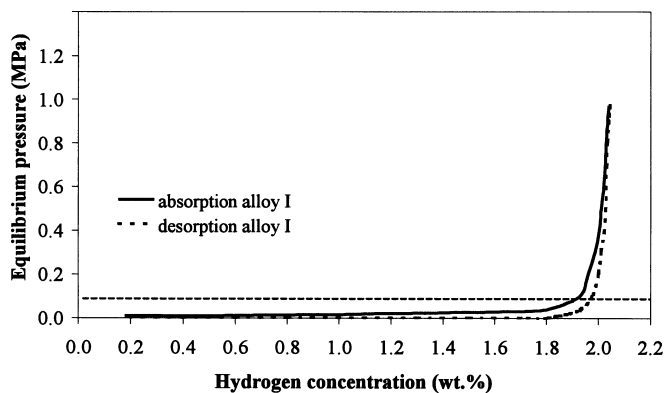


Fig. 5. Pressure-composition isotherm for absorption/desorption of hydrogen from the gas phase using ($Zr_{0.5}Ti_{0.5}$)($V_{0.8}Mn_{0.8}Cr_{0.4}$) at 293 K

cell with $(Zr_{0.5}Ti_{0.5})(V_{0.8}Mn_{0.8}Cr_{0.4})_{2-x}Ni_{0.4+x}$ alloys, we observed increasing amounts of Mn ions in the electrolyte solution upon cycling. This problem is being evaluated in detailed studies. At the present stage of investigation we assume that the changes in the chemical composition of the alloy electrode are one of the factors responsible for the cyclic performance of the alloy electrode in the closed cell. Gao et al. [7] examined the electrochemical behaviour of $ZrV_{0.2}Mn_{0.6}$, $ZrV_{0.2}Mn_{0.6}Cr_{0.1}Ni_{1.2}$ and $ZrTi_{0.1}V_{0.2}Mn_{0.6}Co_{0.1}Cr_{0.1}Ni_{1.2}$ Laves phase alloys. The authors have attributed the decrease in capacity of the alloys in a half-cell during cycling in KOH solution to dissolution of vanadium and manganese owing to the increased surface area affected by the pulverization of alloy particles.

Conclusions

Among $AB_{2.4}$ alloys in which iron is one of the components of group B, $(Zr_{0.35}Ti_{0.65})(V_{1.33}Cr_{0.4}Fe_{0.27})_{2-x}Ni_{0.4+x}$, the highest discharge capacities were found for alloys II C (240 mAh/g) > II Ca (218 mAh/g) > II Cb (215 mAh/g). From the formulas corresponding to these alloys [$(Zr_{0.35}Ti_{0.65})(V_{0.93}Cr_{0.28}Fe_{0.19}Ni_{1.0})$, $(Zr_{0.35}Ti_{0.65})(V_{1.0}Cr_{0.30}Fe_{0.20}Ni_{0.9})$, $(Zr_{0.35}Ti_{0.65})(V_{0.86}Cr_{0.26}Fe_{0.18}Ni_{1.1})$, respectively], it can be inferred that the optimum contribution of nickel in group B is in the range $x = 0.5-0.7$. The increase in capacity for these alloys is parallel to the increase in the hydrogen concentration determined from both PCT and EPC isotherms. Of the three alloys,

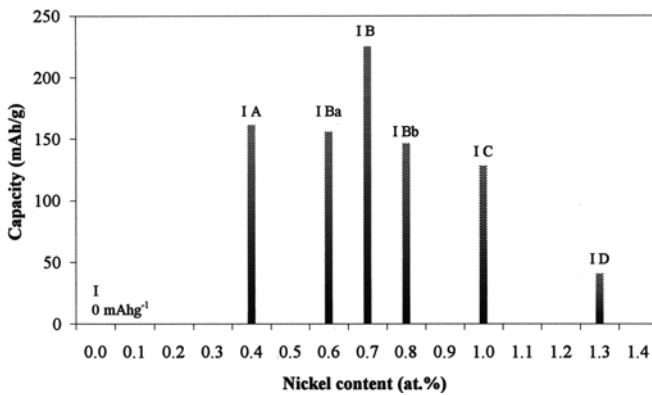


Fig. 6. The influence of nickel content on the discharge capacity of $(Zr_{0.5}Ti_{0.5})(V_{0.8}Mn_{0.8}Cr_{0.4})_{2-x}Ni_{0.4+x}$ at 293 K

Table 4. Chemical compositions and discharge capacities for hydrogen absorbing alloys of general formula $(Zr_{0.5}Ti_{0.5})(V_{0.8}Mn_{0.8}Cr_{0.4})_{2-x}Ni_{0.4+x}$

Symbol of alloy	Chemical composition	Discharge capacity (mAh/g alloy)
I Ba	$(Zr_{0.5}Ti_{0.5})(V_{0.72}Mn_{0.72}Cr_{0.36}Ni_{0.6})$	156
I B	$(Zr_{0.5}Ti_{0.5})(V_{0.68}Mn_{0.68}Cr_{0.34}Ni_{0.7})$	225
I Bb	$(Zr_{0.5}Ti_{0.5})(V_{0.64}Mn_{0.64}Cr_{0.32}Ni_{0.8})$	146

the unit cell volume is the highest for sample II C which provides the highest capacity. It is interesting to note that alloy II A, of which the unit cell volume exceeds

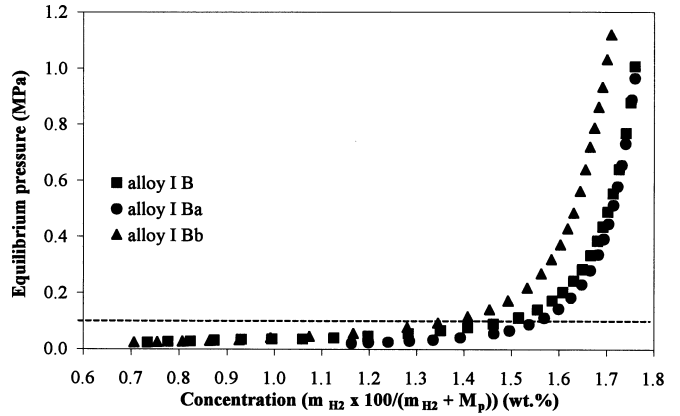


Fig. 7. Pressure-composition isotherms for absorption/desorption of hydrogen from the gas phase using $(Zr_{0.5}Ti_{0.5})(V_{0.8}Mn_{0.8}Cr_{0.4})_{2-x}Ni_{0.4+x}$ at 293 K (m_{H_2} =mass of absorbed hydrogen, M_p =mass of sample)

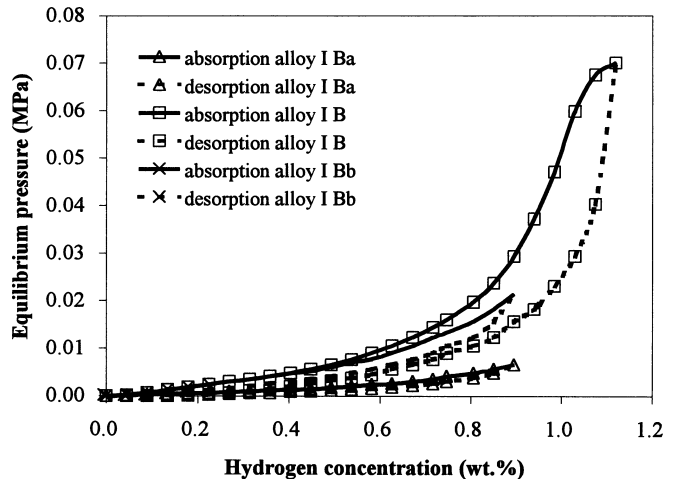


Fig. 8. Electrochemical pressure-composition isotherms for absorption and desorption of hydrogen using $(Zr_{0.5}Ti_{0.5})(V_{0.8}Mn_{0.8}Cr_{0.4})_{2-x}Ni_{0.4+x}$ at 293 K

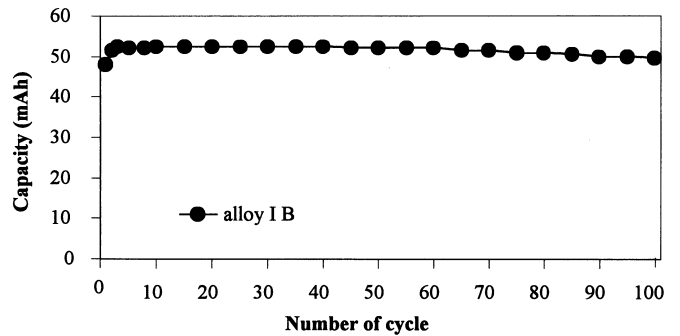


Fig. 9. Durability of the button cell with a negative electrode made of alloy I B, $(Zr_{0.5}Ti_{0.5})(V_{0.68}Mn_{0.68}Cr_{0.34}Ni_{0.7})$

the values of the other alloys listed in Table 1, is quite inactive (capacity 0 mAh/g). From this comparison the conclusion can be drawn that the size of the unit cell plays a role in electrochemical sorption/desorption process electrodes only in the case of samples containing the optimum content of nickel. The problem remaining for further investigation is why sample II C of the highest capacity measured in an open cell exhibits unsatisfactory life cycle performance in a closed cell (Fig. 4).

Considering alloys $AB_{2.4}$ containing manganese in group B, $(Zr_{0.5}Ti_{0.5})(V_{0.8}Mn_{0.8}Cr_{0.4})_{2-x}Ni_{0.4+x}$, it was shown that no hydrogen could be inserted electrochemically in alloy free of nickel (sample I), despite good sorption/desorption characteristics in the gas/solid system (Fig. 5). Such a behaviour changed after adding nickel. The presence of nickel resulted in a decrease in the unit cell volumes of the modified alloys (Table 3). The lowest discharge capacity was found for the alloy $(Zr_{0.5}Ti_{0.5})(V_{0.44}Mn_{0.44}Cr_{0.22}Ni_{1.3})$, denoted I D, with the lowest unit cell volume and the highest amount of nickel (Fig. 6, Table 3). Three alloys $[(Zr_{0.5}Ti_{0.5})(V_{0.72}Mn_{0.72}Cr_{0.36}Ni_{0.6})]$, sample I Ba, $(Zr_{0.5}Ti_{0.5})(V_{0.68}Mn_{0.68}Cr_{0.34}Ni_{0.7})$, sample I B, and $(Zr_{0.5}Ti_{0.5})(V_{0.64}Mn_{0.64}Cr_{0.32}Ni_{0.8})$, sample I Bb], in which the nickel contents in group B corresponded to $x=0.2$, $x=0.3$ and $x=0.4$, respectively, but their unit cell volumes differed insignificantly (Table 3), were characterized by the PCT, EPC and electrochemical charge/discharge measurements. PCT curves (Fig. 7) show a significantly lower concentration of hydrogen in sample I Bb. The hydrogen concentrations in the alloys evaluated from PCT isotherms changed in the following order: I Ba \geq I B > I Bb. EPC isotherms (Fig. 8) proved the highest concentration of hydrogen in sample I B, whereas sample I Ba sorbed less hydrogen. From this compari-

son it is clear that the sorption/desorption process occurring in an electrochemical system strongly depends on the nickel content of the alloy. Sample I B, $(Zr_{0.5}Ti_{0.5})(V_{0.68}Mn_{0.68}Cr_{0.34}Ni_{0.7})$, exhibited the highest discharge capacity in an open cell. From Fig. 8 one can observe that for samples I Ba and I Bb, containing less and more nickel than sample I B, hydrogen is sorbed only up to a concentration of about 0.9 wt.%, whereas the concentration of hydrogen in sample I B is as high as 1.1 wt.%. Moreover, the latter alloy sorbs hydrogen at significantly higher pressure. This fact can be related to a good cyclic behaviour of this alloy as tested in a closed cell. The loss of capacity upon cycling observed in Fig. 9 is assumed to arise from the escape of manganese from the alloy electrode to the electrolyte.

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References

1. Kopczyk M, Wójcik G, Młynarek G, Sierczyńska A, Betowska-Brzezińska M (1996) *J Appl Electrochem* 26:639
2. Wójcik G, Kopczyk M, Młynarek G, Majchrzycki W, Betowska-Brzezińska M (1996) *J Power Sources* 58:73
3. Sievert A, Gatta A (1928) *Z Anorg Chem* 172:1
4. Kleperis J, Wójcik G, Czerwiński A, Skowroński J, Kopczyk M, Betowska-Brzezińska M (2001) *J Solid State Electrochem* 5:229
5. Sakai T, Muta K, Miyamura H, Kuriyama N, Ishikawa H (1992) In: Corrigan DA, Srinivasan S (eds) *Proceedings of the symposium on hydrogen storage materials, batteries and electrochemistry*. (Electrochemical Society series, vol 92-5) The Electrochemical Society, Pennington, NJ, p 59
6. Iwakura Ch, Matsuoka M (1991) *Prog Batt Mater* 10:81
7. Gao X-P, Sun Y-M, Toyoda E, Higuchi E, Nakagima T, Suda S (2000) *Electrochim Acta* 45:3099