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POLARIZATION CHARACTERISTICS AND CATHODIC HYDROGENATION OF TbNi_{4.8}M_{0.2} (M = Sb, Bi, Al) ALLOYS IN STRONG ALKALINE SOLUTION

CHARAKTERYSTYKI POLARYZACYJNE ORAZ KATODOWE WODOROWANIE STOPÓW TYPU TbNi_{4.8}M_{0.2} (M = Sb, Bi, Al) W SILNIE ALKALICZNYM ROZTWORZE

In this work an initial characterisation of electrochemical polarization behaviour of TbNi_{4.8}M_{0.2} (M = Sb, Bi or Al) type alloys in strong alkaline solution has been carried out. It was established that all the tested TbNi_{4.8}M_{0.2} alloys passivated in 6 M KOH. It is shown that the presence of Bi in the hydrogenated alloy causes distinct increase of anodic current in passive range and thus worsens the passivating properties of the alloy. Polarization resistance of the tested alloys measured at potentials close to equilibrium potential of H₂O/H₂ system allowed to evaluate exchange current densities for hydrogen absorption-desorption process. Absorption efficiency of cathodically evolved hydrogen on TbNi_{4.8}M_{0.2} type alloys in strong alkaline solution has been investigated at $p = 1$ atm by the potentiostatic technique. The hydrogen charging and discharging experiments have shown that the tested alloys absorb hydrogen effectively in strong alkaline solution, and TbNi_{4.8}Bi_{0.2} alloy is capable to absorb the highest quantities of cathodic hydrogen.

W pracy dokonano elektrochemicznej charakterystyki polaryzacyjnej stopów typu TbNi_{4.8}M_{0.2} (M = Sb, Bi lub Al) w środowisku silnie alkalicznym. Stwierdzono, że wszystkie badane stopy TbNi_{4.8}M_{0.2} pasywują się w 6 M KOH. Obecność bizmutu w badanym stopie prowadzi do wzrostu gęstości prądów anodowych, a tym samym pogarsza odporność korozyjną stopu. Opór polaryzacji badanych stopów wyznaczony dla potencjału bliskiego potencjałowi równowagowemu układu H₂O/H₂ pozwolił ocenić gęstości prądów wymiany dla procesu absorpcji/desorpcji wodoru. Stosując potencjostatyczną metodę pomiaru, badano absorpcję katodowo wydzielanego wodoru przez wyżej wymienione stopy w silnie alkalicznym roztworze. Pomiarzy ładowania i rozładowania pokazują, że wszystkie stopy TbNi_{4.8}M_{0.2} absorbują wodór, przy czym największą efektywnością pochłaniania katodowego wodoru pod ciśnieniem 1 atm charakteryzuje się TbNi_{4.8}Bi_{0.2}.

1. Introduction

In recent years intermetallic compounds and alloys of RT₅ type (where R = rare-earth element, T – transition metal) have found their wide application, mainly as anodic materials for reversible, NiMH hydride batteries [1-4]. The NiMH type batteries possess many unique properties, including high capacities and high rates of charge/discharge processes. Moreover, owing to relatively small quantities of toxic metals in their composition, they are considered to be environmentally friendly.

As the negative electrode material the RT₅ alloys are the most frequently used in NiMH batteries. The parent alloy: LaNi₅ absorbs ca 1.5 mass % of hydrogen, however, its hydrogen capacity unfavourably decreases during successive charge/discharge cycles. Decrease of capacity

is accompanied with alloy pulverization and oxidation of lanthanum in alkaline solution to produce La(OH)₃ [5-7]. In order to improve hydrogen storage abilities of LaNi₅ alloy, numerous attempts of modification of its chemical composition (partial substitution of both La and/or Ni) are being taken up. Attempts with so called “mishmetal” in place of La appeared to have been not very promising [8, 9]. Similarly, substitution of light lanthanides for La did not result in improvement of alloy hydrogenation properties. In literature do not exist data relating hydrogen absorption ability of RT₅ type alloys containing heavy lanthanides (with electron configuration $4f^9 - 4f^{14}$), e.g. terbium (Tb).

The purpose of the present paper is an initial evaluation of usefulness of new ternary TbNi_{4.8}M_{0.2} (M = Al, Bi or Sb) alloys as prospective negative electrode mate-

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rials for NiMH -type batteries in view of their electrochemical corrosion properties and their ability to absorb cathodically evolved hydrogen.

2. Experimental

Electrochemical tests have been carried out for alloys with the following chemical formulae: $\text{TbNi}_{4.8}\text{Al}_{0.2}$, $\text{TbNi}_{4.8}\text{Bi}_{0.2}$ and $\text{TbNi}_{4.8}\text{Sb}_{0.2}$. The alloys have been prepared by arc melting of stoichiometric amounts of high-purity ($\geq 99.9\%$) elements: Tb, Ni, Sb, Bi and Al (Aldrich Chem. Company Inc.).

Potentiostatic measurements have been carried out in classic three-electrode system cell using CHI 1140A electrochemical station (CH Instruments, Austin, Texas – USA). Working electrodes had a shape of rotating discs with an operating surface area of $0.05 - 0.09 \text{ cm}^2$. As test solution 6 M KOH aqueous solution has been applied. The test solution was deaerated during each experiment by passing high-purity argon with a rate of 10 L/h and thermostated ($25 \pm 0.1^\circ\text{C}$).

The potentiodynamic polarization curves were measured from cathodic ($E_{\text{start}} = -1.50 \text{ V}$) to anodic ($E_{\text{end}} = +0.7 \text{ V}$) potential with a scan rate of $0.01 \text{ V} \cdot \text{s}^{-1}$. All electrode potentials were measured and are expressed versus saturated calomel electrode (SCE). In order to avoid surface screening by gas bubbles potentiodynamic curves were registered at fast rotation speed of the disc electrode: $10 \text{ rev} \cdot \text{s}^{-1}$. The auxiliary electrode was made of platinum wire. Before each polarisation test the operating surface of corresponding electrodes has been polished on waterproof emery papers (up to No 1000 grade), then washed with water, alcohol and eventually dried.

The potentiostatic charge/discharge measurements were carried out according to method described in [10]. The samples were charged cathodically ($i_c = -1.0 \text{ mAcm}^{-2}$, $t = 600 \text{ s}$) in 6 M KOH solution and then, immediately polarised anodically ($E_a = -0.20 \text{ V}$). The external anodic current (i_a) registered at -0.20 V is a sum of oxidation rate of absorbed hydrogen (i_H) and alloy oxidation rate (dissolution and passivation), equal to i_M . The rate of anodic process connected with metal oxidation have been determined for individual alloys in separate experiments, using hydrogen-free samples.

3. Experimental results and discussion

3.1. Potentiodynamic polarisation curves

In Fig. 1 potentiodynamic polarization curves of three tested $\text{TbNi}_{4.8}\text{M}_{0.2}$ type alloys in 6 M potassium

hydroxide solution are presented. As it results from Fig. 1, the potentiodynamic characteristics are similar for Al and Sb containing alloys in strongly cathodic range (-1.5 to -1.2 V) and in the range of oxygen evolution ($+0.4$ to $+0.7 \text{ V}$). In passive region, anodic currents for Al containing alloy are *ca* 2 times greater than these for Sb containing alloys. These two alloys show practically the same value of potential corresponding to cathodic/anodic transition (E_{OCP}) equal to -0.96 V . For Bi containing alloy both cathodic and anodic currents are generally one order of magnitude greater and $E_{\text{OCP}} \approx -0.86 \text{ V}$.

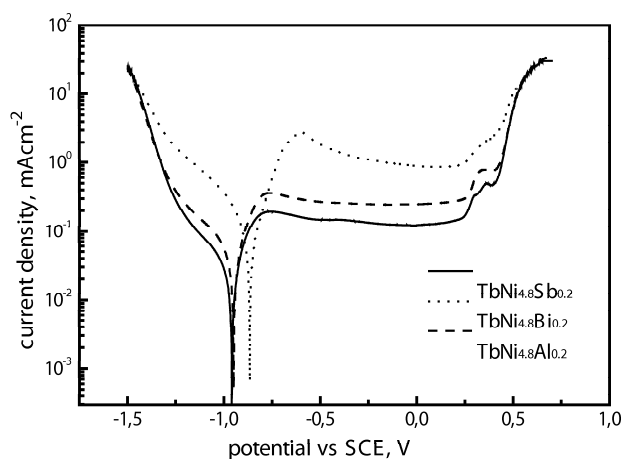


Fig. 1. Potentiodynamic polarization curves of $\text{TbNi}_{4.8}\text{M}_{0.2}$ alloys in 6 M KOH solution (25°C , argon, 10 rps, $0.01 \text{ V} \cdot \text{s}^{-1}$)

For $E < -1.2 \text{ V}$ process of reduction of H_2O molecules is controlled activationally with a Tafel slope $b_c \approx 0.12 \text{ V}$, however, at less negative potentials (-1.2 to -1.0 V) a clear discrepancies from rectilinearity appear in cathodic range. These discrepancies, having form of limiting currents can be presumably attributed to surface development as a result of hydrogenation, and possibly, preferential dissolution of rare-earth metal (Tb). The absolute values of anodic currents in passive region decrease with time and depend on potential scan rate. Moreover, these currents represent not only alloy oxidation (passivation) but oxidation of cathodically absorbed hydrogen as well. To evaluate more thoroughly kinetics of electrode processes within the passive range, the chronoamperometric curves (at $E = \text{const}$) have been determined.

As it is easy to calculate, the equilibrium potential of the $\text{H}_2\text{O}/\text{H}_2$ system is equal to -1.13 V versus SCE (assuming $\text{pH} = 15$ and $p_{\text{H}_2} = 1 \text{ atm}$). From Fig. 2 it results that cathodic/anodic transfer corresponds to potentials from -0.96 V to -0.86 V for all of the tested alloys.

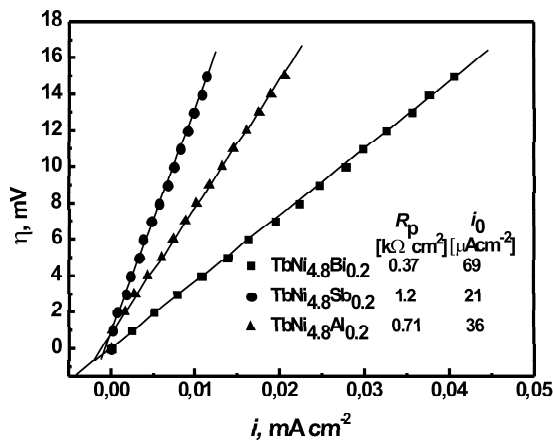


Fig. 2. External current changes as an effect of polarization from E_{H_2O/H_2}^{eq} up to 15 mV in anodic direction. The slope of straight lines is a measure of polarization resistance (6 M KOH, argon, 25°C)

It has to be stressed that the cathodic/anodic transfer potential is not a corrosion potential and it should be ascribed to the equilibrium of H_2O/H_2 system on the tested electrodes. Thus, the hydrogen absorbed in cathodic region is oxidized above $E_{H_2O/H_2}^{eq} = -1.13$ V. This way, analysis of $\partial\eta/\partial i$ changes in the vicinity of the equilibrium potential allows to determine the exchange current densities for the H_2O/H_2 system. The exchange current density for the hydride electrode reaction can be used to characterize the electrocatalytic activity for the charge-transfer at the metal/electrolyte interface [11]. According to Notten and Hokkelling [11], the exchange current density (i_0) can be calculated from the polarization resistance (R_p) determined by Stern-Geary method [12]:

$$R_p = \left(\frac{\partial\eta}{\partial i} \right)_{E \rightarrow OCP} = \frac{RT}{Fi_0}, \quad (1)$$

where the RT/F fraction is equal to 25.7 mV for 298 K. The $\eta = f(i)$ linear polarization data of the TbNi_{4.8}M_{0.2} alloys together with calculated R_p and i_0 values are presented in Fig. 2. As one should expect, partial substitution of Ni with Bi causes significant increase of exchange current for H_2O/H_2 system, which reflects the fast hydrogen absorption/desorption process. Comparison of i_0 values with anodic current densities in the passive region allows to conclude that main reason of improvement of surface catalytic properties in relation to H_2O/H_2 system can be limited passivation of Bi substituted alloy after its hydrogenation.

3.2. Evaluation of hydrogen absorption ability by TbNi_{4.8}M_{0.2} alloys

In Fig. 3 (a-c) the typical plots of anodic currents versus exposure time recorded at $E = -0.2$ V for hydrogen-free samples (i_M) and for samples after their

hydrogenation (i_a) are presented. At it has been mentioned earlier, the measured external anodic current i_a is a sum of two components [9, 13]:

$$i_a = i_H + i_M \quad (2)$$

where i_H is the current corresponding to the oxidation of hydrogen atoms desorbing from the specimen, and i_M is the current related to other possible anodic processes: dissolution and/or passivation of the alloy constituents.

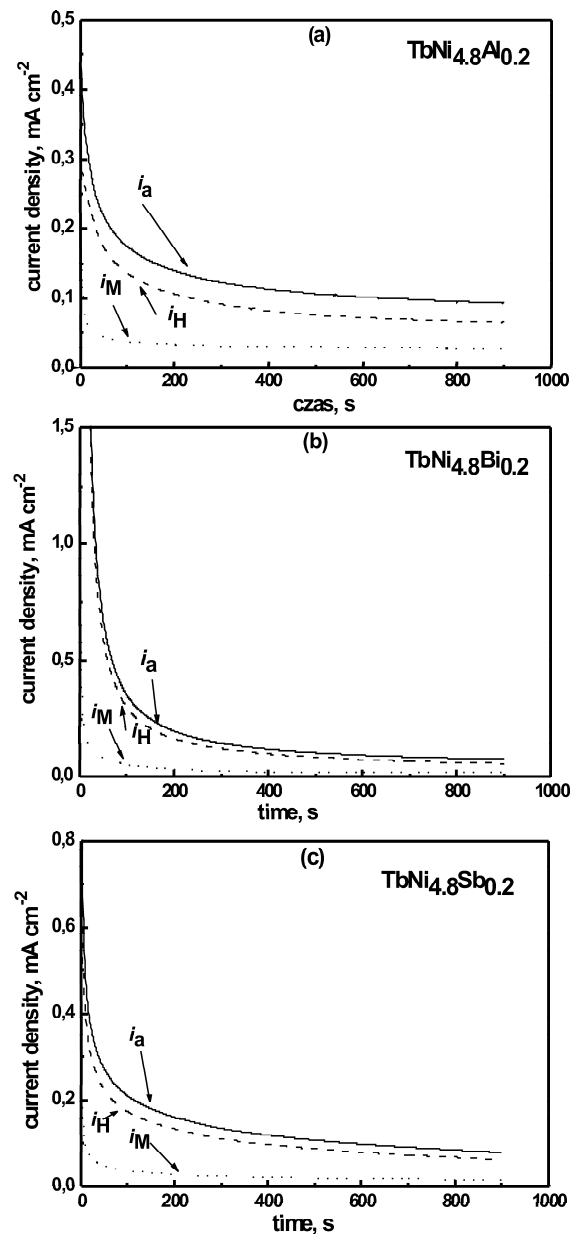


Fig. 3. Chronoamperometric curves of TbNi_{4.8}Al_{0.2} (a), TbNi_{4.8}Bi_{0.2} (b) and TbNi_{4.8}Sb_{0.2} (c) at $E_a = -0.2$ V in 6 M potassium hydroxide solution. Doted line (i_M) represents hydrogen-free sample, dashed line (i_H) the oxidation of hydrogen atoms desorbing from the specimen, and solid line (i_a) – external anodic current of the sample after its cathodic hydrogenation

Currents of alloys have been determined in separate experiments on the hydrogen-free specimens. The anodic current of hydrogen oxidation (i_H) being a measure of the overall hydrogen desorption rate, has been calculated for particular sample by subtracting the current i_M from the current i_a . During cathodic charging in 6 M KOH solution at $|i_c| = 1 \text{ mAcm}^{-2}$ for $t_{\text{char}} = 600 \text{ s}$, the amount of evolved hydrogen expressed by charge density is equal to $q_{H^+, \text{red}} = 600 \text{ mCcm}^{-2}$. Integration of i_H currents over the time range necessary for their settling down (Fig. 3 (a-c)) allows to evaluate the amount of hydrogen absorbed by the specimen during cathodic exposure. Figure 4 shows the actual amounts of absorbed hydrogen represented by charge density ($q_{H, \text{ox}}$) as a function of discharge time for the tested alloys. As it results from Fig. 4, in potentiostatic conditions ($E = -0.2 \text{ V}$), the quantity $q_{H^+, \text{ox}}$ tends to settle down at practically constant level after ca 900 s.

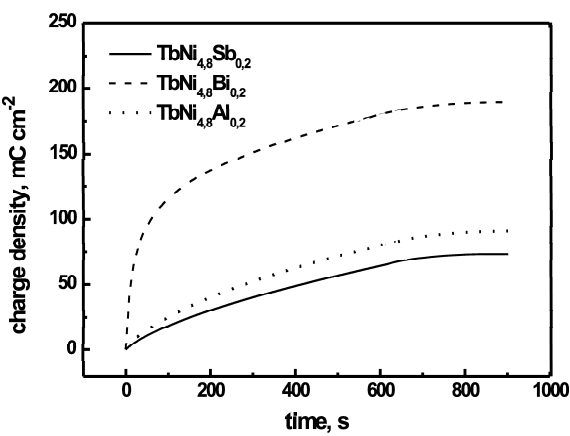


Fig. 4. Amounts of cathodically absorbed hydrogen presented as charge density of hydrogen oxidation ($q_{H, \text{ox}}$) versus desorption time for the tested materials

The effectiveness for absorption of cathodically evolved hydrogen can be expressed by the following equation [13, 14]:

$$x_{\text{eff}} = \frac{q_{H, \text{ox}}}{q_{H^+, \text{red}}} \tag{3}$$

TABLE 1
The efficiency for absorption of cathodically evolved hydrogen for the tested alloys

Alloy formula	x_{eff}
TbNi _{4.8} Al _{0.2}	0,14
TbNi _{4.8} Sb _{0.2}	0,17
TbNi _{4.8} Bi _{0.2}	0,33

The calculated values of x_{eff} for the tested alloys are presented in Table 1. The obtained coefficients indicate

that the TbNi_{4.8}Bi_{0.2} absorbs distinctly more of cathodic hydrogen than the two remaining alloys.

It should be stressed that analogous positive effect of bismuth on hydrogen absorption ability has been found in our previous papers for LaCo_{4.8}M_{0.2} (M = Al, Bi or Sb) [10], ZrNi_{4.8}M_{0.2} (M = Al + Li, Bi or Sb) [15] and for LaNi_{4.8}M_{0.2} (M = Bi, Sb or Mg) alloys [16]. The chances are that bismuth actively participates in the process of hydrogen absorption/desorption. It is possible that it forms non-stable intermediate product (e.g. BiH₃) that accelerates and facilitates the hydrogenation of the alloy.

4. Conclusions

- All the tested TbNi_{4.8}M_{0.2} (M = Al, Bi or Sb) alloys are capable to absorb cathodically evolved hydrogen in strongly alkaline solution. The effectiveness of hydrogenation is particularly distinct for Bi containing alloy.
- The TbNi_{4.8}M_{0.2} alloys passivate in 6 M KOH solution in wide range of potentials which is advantageous from corrosion resistance point of view. On the other hand, presence of bismuth in the alloy clearly increases anodic currents in passive region. However, limited tendency of TbNi_{4.8}Bi_{0.2} alloy to passivation is prone to acceleration of partial electrode processes of H₂O/H₂ system.

Acknowledgements

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