Estimation of Diffusion-Kinetic and Thermodynamic Properties of Al-Sm-H Alloys

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Abstract

Metal hydride systems for hydrogen storage are now commercially manufactured and the demand for them is constantly growing. Metal hydrides have the following features: a unique combination of properties of metal-hydrogen systems; extremely high volumetric densities of hydrogen atoms in the metal matrix; a wide range of operating pressures and temperatures; the selectivity of the hydrogen absorption process; significant changes in the physical properties of the metal when it is saturated with hydrogen; their catalytic activity, etc. The purpose of our research was to study the effect of the temperature of cathodic polarisation on the diffusion-kinetic, thermodynamic, and physical properties of Al-Sm-H alloys.

In our study we used electrodes of Al-Sm-H alloys obtained electrochemically using cathodic intercalation from a 0.5 M dimethylformamide solution of samarium salicylate at $E_{cp} = -2.9$ V (relative to the non-aqueous silver chloride electrode) and the temperature of 25 °С for 1 hour. We used the electromotive force method to determine the thermodynamic properties: Gibbs free energy ($\Delta G$), entropy ($\Delta S$), and enthalpy ($\Delta H$). The potentiostatic method was used to calculate the diffusion-kinetic properties: intercalation constants, adsorption, switching current density, and the diffusion coefficient. The microstructural analysis allowed us to determine the effect of the temperature on the changes in the surface morphology.

The study showed that an increase in the temperature results in an increase in $\Delta G$, $\Delta S$, and $\Delta H$, which means that at higher temperatures the degree of the system disorder increases. Nevertheless, the calculated characteristics comply with the existing literature.

Keywords: electromotive force method, rare earth elements, aluminum matrix, hydrogen, potentiostatic method, microstructure, diffusion-kinetic characteristics.

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1. Introduction

The annual depletion of fossil fuels coupled with global environmental problems makes it necessary to search for alternative energy sources which are renewable and environmentally friendly and will last hundreds of years [1]. Modern science views hydrogen as one of the alternative energy sources [2–9]. Advancement in hydrogen technologies and development of hydrogen fuel cells make it possible to use hydrogen fuel in autonomous energy sources, both mobile and stationary. Compact and safe hydrogen storage is a vital problem which plays a key role in the development of a hydrogen economy.

All of this determines the main application areas of hydrides of intermetallic compounds [10–15], which are the following: stationary hydrogen storage, on-board hydrogen storage and hydrogen transportation, hydride compressors, hydrogen getters, hydrogen separation and purification, separation of hydrogen isotopes, heat pumps, refrigerators, and hydride dispergation.

Metal hydride systems for hydrogen storage are commercially manufactured and the demand for them is growing, slowly but steadily. Metal hydrides have the following features: a unique combination of properties of metal-hydrogen systems; extremely high volumetric densities of hydrogen atoms in the metal matrix; a wide range of operating pressures and temperatures; the selectivity of the hydrogen absorption process; significant changes in the physical properties of the metal when it is saturated with hydrogen; the catalytic activity, etc.

Due to their technological flexibility, high compactness, safety, and energy efficiency, metal-hydride hydrogen storage materials are very promising and can be used in the production of efficient combined systems for hydrogen storage.

Among the most promising materials used in the hydrogen economy are alumohydrides as they have high volumetric and mass density [21–23].

The purpose our research was to study the influence of the temperature of cathodic polarisation on the diffusion-kinetic and physical properties of Al-Sm-H alloys.

2. Experimental

The matrix of the Al-Sm alloy was obtained electrochemically on aluminium foil electrodes (99.99) (GOST 11069-74) using cathodic intercalation [24] from a 0.5 M dimethylformamide (DMF) solution of samarium salicylate at $E_\text{cp} = -2.9$ V (relative to the non-aqueous silver chloride electrode) and the temperature of 25 °C for 1 hour. The Al-Sm-H electrodes were obtained using pulse potentiostatic method at $E_\text{cp} = -1.6$ V for 30 minutes from the DMF: H$_2$O solution with the volume ratio (7 : 3) and the temperature of 25 °C. The duration of the initial short pulse was 800 milliseconds.

The diffusion-kinetic properties were determined using the potentiostatic method. Potentiostatic cathodic polarisation was performed at the potential $E_\text{cp} = 1.6$ V for half an hour within the temperature range from 303.15 to 333.15 K, using a Р-20X potentiostat from Electrochemical Instruments (Russia) together with the software provided by the manufacturer. We used a BT8-2 thermostat from Termex (Russia) to maintain the temperature with a precision of up to ± 0.1 °C.

Hydrogen was intercalated into the Al-Sm alloy previously obtained on an aluminium electrode. The intercalation characterises the duration of the electrochemical discharge stage accompanied by the formation of the Al-Sm-H interstitial phase. We assume that hydrogen intercalation proceeded according to the reaction (1):

$$\text{Al-Sm} + x\text{H}^+ + xe^- \rightarrow \text{Al-Sm-H}_x.$$  

The diffusion-kinetic properties were calculated using the methodology described in [25–27].

The amount of extracted oxygen was determined by integrating the $i$ - $t$ curve minus the electric charge [28]. The electric charge was determined by multiplying the residual current by the extraction time ($t_e$):

$$Q'_H = \int idt - i_{\phi} t_e,$$  

where $Q'_H$ is the electric charge spent on the oxidation of the extracted hydrogen and $i_{\phi}$ is the residual current.

The total electric charge ($Q_H$) corresponding to the hydrogen absorbed by a surface unit during the chemical deposition was determined using equation (3):

$$Q_H = Q'_H / S,$$  

where $S$ is the surface area of the electrode.
where $S$ is the area of the working surface of the electrode during the extraction.

The processes occurring during the discharge of the studied electrode were determined based on the changes in the system’s thermodynamic properties during reactions (4), (5), and (6):

$$\Delta G(x, T)_p = -E_p \cdot F,$$

$$\Delta S(x, T)_p = F \left( \frac{dE}{dT} \right)_p,$$

$$\Delta H = \Delta G + T \cdot \Delta S.$$ (6)

The dependence $i - 1/T$ was used to determine the activation energy according to equation (7):

$$A = -2.3R \left[ \frac{a \log i}{\Delta(1/T)} \right]_n = -2.3R \left[ \frac{\log i - \log i_0}{1/T_2 - 1/T_1} \right]_n.$$ (7)

We used an AGPM–6M FULK 401163.001-01 microstructure image analyser to control and visualise the information about the linear dimensions of the microobjects and the shape of the microparticles, as well as to create an archive of microobjects. The porosity was measured using the Mikroshlif software.

5. Results and discussion

The potentiostatic study demonstrated that during the initial stage of the hydride layer formation in the Al-Sm electrode, the dependence $i-t$ (Fig. 1) is presented as a linear plot of $i-1/t$ (Fig. 2b). This indicates the presence of the limiting stage of hydrogen diffusion in the Al-Sm alloy at the set potential and temperature.

0.5–10 seconds later, the current drop slows down dramatically (Fig. 2a, b), and the nuclei of a new phase begin to grow. This results in the formation of a continuous hydride layer. About 20 minutes later the current density $i$ on the electrode stops changing with time, and the hydride layer continues growing due to the chemical interaction between the hydrogen and the elements of the Al-Sm alloy (Table 1). The value of the steady-state current $i_{st}$ increases, when the cathodic polarisation potential sweeps to more negative values.

The diffusion-kinetic properties of the electrochemical intercalation of hydrogen into the Al-Sm alloy at various cathodic polarisation potentials were studied using pulse potentiostatic method at $E_{cp} = -1.6 \text{ V}$ for 30 minutes. The initial pulse was $\tau = 1 \text{ s}$.

![Fig. 1. Influence of the temperature on the $i, t$ curves during hydrogen sorption by the Al-Sm alloy in aqueous organic electrolyte ($V_{H_2O} : V_{DMF} = 7 : 3$) for 30 minutes at the cathodic polarisation potential $-E_{cp} = 1.6 \text{ V}$ and the temperatures: 1 – 303.15; 2 – 313.15; 3 – 323.15; 4 – 333.15 K](image-url)
The analysis of the dependence of the \( i-t \) curves (Fig. 1) of hydrogen intercalation into the Al-Sm alloy in the coordinates \( i-\sqrt{t} \) (Fig. 2a), \( i-1/\sqrt{t} \) (Fig. 2b) allowed us to calculate the intercalation constant \( K_{int} \), \( C_o\sqrt{D} \), the switching current being \( i_{t=0} \).

The calculated diffusion-kinetic properties are presented in Table 2.

In the binary Al-Sm system, consisting of a hydride-forming metal (aluminium) and a rare-earth metal (REM) catalysing the hydride formation, it is possible to partially substitute some elements with others, since the interaction between metals is accompanied by the formation of intermetallic compounds, which allows for better hydride formation. The desorption of hydrogen from MAI\( _4 \) alumohydrides (where M = Li, Na, K, P33) includes several stages and proceeds by means of chemical decomposition. As a result, 2 wt% hydrogen is released [29]. This changes the rate of the interaction with hydrogen.

According to the results presented in Table 2 the rate of the sorption of hydrogen by the aluminium-samarium matrix increases with the increase in temperature. This is indicated by the diffusion-kinetic properties: the intercalation constants \( K_{int} \) and \( C_o\sqrt{D} \) increase by about 2.0 times, the adsorption \( \Gamma \) and the current density \( i_{t=0} \) increase by about 2.1 times, and the diffusion coefficient \( D \) increases by 1.27 times.

### Table 1. Influence of the temperature on the nucleation process on the Al-Sm-H-electrode

<table>
<thead>
<tr>
<th>Temperature (( T )), K</th>
<th>Electric charge (( Q \cdot 10^3 )), A·s/cm²</th>
<th>Number of nuclei (( N \cdot 10^{-11} ))</th>
<th>Weight of nuclei (( m \cdot 10^{-18} )), g</th>
<th>Radius of nuclei (( r ), nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303.15</td>
<td>2.45</td>
<td>10.72</td>
<td>0.21</td>
<td>1.53</td>
</tr>
<tr>
<td>313.15</td>
<td>5.46</td>
<td>2.13</td>
<td>2.24</td>
<td>4.43</td>
</tr>
<tr>
<td>323.15</td>
<td>7.52</td>
<td>1.19</td>
<td>6.18</td>
<td>4.73</td>
</tr>
<tr>
<td>333.15</td>
<td>10.22</td>
<td>0.61</td>
<td>15.52</td>
<td>6.32</td>
</tr>
</tbody>
</table>

### Table 2. Diffusion-kinetic properties of the Al-Sm alloy

<table>
<thead>
<tr>
<th>Temperature (( T )), K</th>
<th>Intercalation constant (( K_{int} \cdot 10^5 )), A·cm²/s^{1/2}</th>
<th>Diffusion component (( C_o\sqrt{D} \cdot 10^{10} )), mol/²·cm²</th>
<th>Steady-state current density (( i_{t=0} )), mA/cm²</th>
<th>Adsorption value (( \Gamma \cdot 10^6 )), mol/cm²</th>
<th>Chemical diffusion coefficient of the intercalated particles (( D \cdot 10^{12} )) cm²/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>303.15</td>
<td>6.444</td>
<td>1.182</td>
<td>0.061</td>
<td>0.842</td>
<td>2.64</td>
</tr>
<tr>
<td>313.15</td>
<td>8.527</td>
<td>1.564</td>
<td>0.073</td>
<td>0.961</td>
<td>3.06</td>
</tr>
<tr>
<td>323.15</td>
<td>9.882</td>
<td>1.813</td>
<td>0.084</td>
<td>1.283</td>
<td>3.56</td>
</tr>
<tr>
<td>333.15</td>
<td>13.011</td>
<td>2.386</td>
<td>0.133</td>
<td>2.351</td>
<td>3.54</td>
</tr>
</tbody>
</table>
The thermodynamic properties of the formed structures were determined using the electromotive force method (EFM) based on the stationary potential values. The thermodynamic properties of hydride formation in the aluminium-samarium alloy are given in Table 3.

According to (4), the activation energy is 39.755 kJ/mol. This means that the process is limited by the discharge stage or by a chemical reaction.

According to Table 2, values of $\Delta G$, $\Delta S$, and $\Delta H$ increase following the growth of temperature, which means that at higher temperatures the degree of the system disorder increases. The calculated characteristics comply with the existing literature. The mean values $\Delta G = -34.412$ kJ/mol and $\Delta H = -44.040$ kJ/mol show that the system is thermodynamically stable and can function in a wide range of temperatures.

The data regarding $E_{H_2} – T$ presented in Table 3 may indicate the processes taking place in the solid phase of the active substance, as well as the structural transformations in the Al-Sm-H electrode caused by hydrogen intercalation. The conducted experiments demonstrated that all the processes are affected by the temperature. At higher temperatures hydrogen intercalates more deeply.

Taking into account the calculated characteristics, we can say that the temperature coefficient is positive. The correlation between $\Delta G$ and $\Delta H$ determines the sign of the temperature coefficient and helps to evaluate the thermal effect and the nature of the reaction taking place in the system [28]. It also helps to calculate the change in the entropy, which indicates the degree of order in the system. The change is connected with all the interactions between the system’s particles and the structure of the substance [30].

When the coefficient $\Delta E/\Delta T$ is positive, the process is endothermic. By the laws of thermodynamics, the current’s energy in this case is stronger than the thermal effect of the reaction, and the processes within the system are characterised by higher energy costs. Hydrogen intercalation results in significant changes in the structure of the formed compounds.

The analysis of the surface images (Fig. 3, Table 4) demonstrated the presence of rounded entities on the surface of all the studied samples. The formation of the surface structure of the samples is most likely determined by the growth and merging of such entities.

It is also possible to use the electrochemical method to determine the concentration of hydrogen absorbed during the cathodic polarisation of the Al-Sm alloy obtained by means of cathodic intercalation.

The analysis of the dependence of the $i–t$ curves in the coordinates $i–\sqrt{t}$ and $i–1/\sqrt{t}$ demonstrated that the sorption of hydrogen by the Al-Sm alloy is connected to two parallel processes: hydrogen intercalation into the Al-Sm alloy previously formed on the aluminium electrode, and the formation of a new Al-Sm-H interstitial phase. The gradient of hydrogen concentration $dc/dx$ is large enough to ensure the diffusion required for the reaction. The formation of hydrides on the Al-Sm electrode by means of cathodic intercalation proceeds in several stages, which differ in their kinetics and the nature of phases. The first stage involves the formation of a hydrogen solid solution in Al-Sm. In this region, a gradual current drop over time is observed. This corresponds to the process being limited by diffusion, since it is extrapolated to the origin of the coordinates. The second stage involves the formation of crystal nuclei of

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Table 3. Thermodynamic properties of hydride formation in the Al-Sm-H alloy

<table>
<thead>
<tr>
<th>Temperature $(T)$, K</th>
<th>Standard electrode potential $(-E_{st.,(cse)})$, V</th>
<th>Temperature coefficient $(\Delta E/\Delta T \cdot 10^{-1})$, V/K</th>
<th>Average value of the temperature coefficient $(\Delta E/\Delta T \cdot 10^{-1})$, V/K</th>
<th>Standard electrode potential $(-E_{st.})$, V</th>
<th>Gibbs free energy $(-\Delta G)$, kJ/mol</th>
<th>Entropy $(\Delta S)$, kJ/mol K</th>
<th>Enthalpy $-(\Delta H)$, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>303.15</td>
<td>0.576</td>
<td>2.8</td>
<td>2.286</td>
<td>0.553</td>
<td>34.103</td>
<td>27.016</td>
<td>42.284</td>
</tr>
<tr>
<td>313.15</td>
<td>0.579</td>
<td>2.9</td>
<td>2.286</td>
<td>0.556</td>
<td>34.582</td>
<td>27.981</td>
<td>43.114</td>
</tr>
<tr>
<td>323.15</td>
<td>0.582</td>
<td>3.1</td>
<td>2.286</td>
<td>0.559</td>
<td>34.644</td>
<td>29.911</td>
<td>47.241</td>
</tr>
<tr>
<td>333.15</td>
<td>0.585</td>
<td>3.2</td>
<td>2.286</td>
<td>0.562</td>
<td>34.962</td>
<td>30.876</td>
<td>45.551</td>
</tr>
</tbody>
</table>
intermetallic compounds of hydrogen with Al and Sm, and their further growth. This results in the formation of a continuous layer of binary hydrides of the corresponding metals. The third stage involves the growth of the hydride layers of the corresponding metals due to chemical interaction of dissolved hydrogen with the Al-Sm alloy. When the formation of the intermetallic compound on the metallic/intermetallic boundary goes slowly, there is a linear dependence between the rate of the process and the potential.

4. Conclusions

The study determined the diffusion-kinetic and thermodynamic properties of the Al-Sm electrode. It demonstrated that an increase in the temperature of the electrolyte results in higher values of the diffusion-kinetic properties, namely the rate constant, the switching current density, the diffusion rate, and the value of hydrogen adsorption.

The analysis of potentiostatic curves in various coordinates demonstrated that the diffusion process is accompanied by the growth of the hydride layer, which occurs due to the chemical interaction between hydrogen and the elements of the Al-Sm alloy. The rate of hydrogen sorption by the aluminium-samarium matrix increases at higher temperatures. This is indicated by the diffusion-kinetic properties: the intercalation constants $K_{\text{int}}$ and $C_o \sqrt{D}$ increase by about two times, the adsorption $\Gamma$ and the current density $i_{(t=0)}$ increase by about 2.1 times, and the diffusion coefficient $D$ increases by 1.27 times. The study

| Fig. 3. Microstructure of the Al-Sm-H surface and its presentation as a binary (black and white) image using the Mikroshlif software (at $T = 303.15$ K (a, b) and $T = 513.15$ K (c, d))

Table 4. Porosity of the surface layers of the formed alloys of the Al-Sm-H system

<table>
<thead>
<tr>
<th>No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, K</td>
<td>303.15</td>
<td>313.15</td>
<td>323.15</td>
<td>333.15</td>
</tr>
<tr>
<td>Porosity, %</td>
<td>49</td>
<td>16</td>
<td>17</td>
<td>46</td>
</tr>
</tbody>
</table>
showed that an increase in the temperature results in an increase in $\Delta G$, $\Delta S$, and $\Delta H$, which means that at higher temperatures the degree of the system disorder increases. Nevertheless, the calculated characteristics comply with the existing literature.

The highest dispersion was observed in the samples obtained at the temperature of 313.15 K. At a temperature of 313.5–323.15 K the porosity is minimal. However, at 323.15 K the breakdown points appear which become more prominent at 333.15 K.

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Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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