THE INFLUENCE OF LITHIUM TO KINETICS OF HYDROGEN SORPTION BY Li - REE -Al ALLOYS AT TIME CATHODE POLARISATION TO ACID WATER-ORGANIC SOLUTIONS

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Introduction

Alloys like LiLaAl may be used not only as electrodes that are alternative to lithium for lithium and lithium-ion accumulators but also as matrixes for hydrogen sorption.

According to Smith's classification all metals regarding hydrogen are divided into three groups: class metals (where lithium is) that form saltlike hybrids with hydrogen; class of metals (aluminium) that form with hydrogen chemical compounds with covalent bond; lanthanum belongs to the third groups of metals – endo- and exothermic hydrogen absorbent. Thus metallic components of LiLaAl alloy may form a wide range of compounds with hydrogen.

Results and discussions

The aim of this work was to research electrochemical accumulation possibilities of hydrogen with the materials on the base of lithium – lanthanum – aluminium alloys, formed by cathode intercalation method. Influence on the process of hydrogen sorption by electrodes from LiAl, LaAl, LiLaAl alloys after preliminary oxidizing and thermal of aluminium matrix was studied. LiAl, LaAl, LiLaAl alloys were prepared according to cathode incorporation method. Aluminium Grade A 99,99 (Al foil 80mkm thickness or Al wire 3mm diameter) with area of working surface 1cm^2 served as working electrode. Before experiment electrode surface was thoroughly protected by wet glass powder, degreased by spirits, washed in working solution of electrolyte. Lithium incorporation into Al-matrix was carried out at potentiostatic mode at E_{eff}= -2,9V potential for 3 hours from 1M $LiClO_4$ solution in mixture of propylene carbonate and dimethoxyethane solvents 1:1 volume ratio. Water content did not exceed $(3…7)\cdot10^{-3}$ %. For preparation of LaAl alloy, 0,01M solution of lanthanum chloride in dimethyl formamide (DMFA) was used. Potential of lanthanum incorporation was E_{eff} = -2,1V. While LiLaAl electrode formation, a consecutive cathode incorporation of lanthanum and later lithium into Al-matrix at above described conditions was carried out. Al electrode (S= ~10cm^2) was used as a counter-electrode. During a series of experiments with oxidised aluminium the initial surface was exposed to etching in NaOH – 25, Na_2CO_3 – 25 solution (g/l) at t=60°C for 3 minutes with graphite counter-electrodes. The process of further anode oxidising of aluminium was carried out in electrolyte of H_2SO_4 – 140, $H_2C_2O_4$ – 30, La Cl_3 – 0,05 composition (g/l) at potential – 3,0V for 3-5 minutes. The lead plates (S= ~10cm^2) served as counter-electrodes. Heat treatment was produced at 250°C for 2 hours. In experiments of hydrogen electrosorption 0,1M $HClO_4$ water solution in DMFA 1:1 volume ratio was used as a proton-donor media. The process was carried out at E_{eff} = -0,8V. Hydrogen saturation of samples lasted 1-9 hours. A part of electrodes was saturated with hydrogen emitted on the studied electrode, another part - with hydrogen formed on the auxiliary platinum cathode, made as a spiral, inside of which there was a studied electrode. The potential on platinum electrode was the same (-0,8V).

Potentiostatic, galvanostatic, impulse methods and the method of alternating current were used for substantiating of mechanism and kinetics processes on electrodes. All the measurements were carried out by potentiostat P-5848 complete with self-recording potentiometer KSP–4. While carrying out the researches, a three-electrode cell with divided Schott's filters with cathode and anode spaces were used. A bridge of alternating current P-5021 was used for alternating current measurements, a glass-graphite cylinder served as a counter-electrode (S= ~40cm^2) in the centre of which an operating electrode was coaxially placed as a wire (S= ~0,4cm^2). The operating temperature was 298K.

According to the data obtained, preliminary oxidising of Al-base makes lithium incorporation dif-

ficult and thermal treatment on the contrary contributes to increasing of defect concentration on the surface and formation of such a structure of oxide layer which makes the processes of lithium mass transfer easier. Modification of Al-base by lanthanum also contributes to increasing of structure defects of initial aluminium and its electrochemical activity.

Investigations on electrochemical hydrogen incorporation into modified Al electrodes (LiAl, LaAl, LiLaAl) from 0,1M $HClO_4$ water solution with DMFA (1:1) showed that the highest rates of sorption are character for LiLaAl alloys which are richer in lithium – obtained during cathode polarisation which lasted τ_{eff} =6 hours. Preliminary oxidising and thermal treatment make hydrogen incorporation into alloy structure difficult.

While LiAl electrodes saturation with hydrogen with the help of an auxiliary Pt electrode there was also an influence of conditions of electrode surface preliminary treatment. The highest rates of sorption process are fixed on the electrodes which were cathode polarised for 6 hours. The rate of hydrogen saturation of electrodes with an additional Pt cathode increases a lot in comparison with the tests without an additional Pt cathode. Analogous results were obtained for LaAl, LiLaAl electrodes as well.

Conclusions

Investigation of sorption kinetics of hydrogen from water-organic electrolyte ($HClO_4$ + dimethyl formamide) with electrodes from LiAl, LaAl, LiLaAl alloys before and after preliminary oxidising and thermal treatment of Al-base showed that the highest sorption capacity of hydrogen is realised for LiLaAl.

Saturation of formed alloys with hydrogen depends on the amount of lithium intercalated. The highest sorption capacity of hydrogen was fixed for alloys which are richer in lithium. Developed technology of electrochemical material's obtaining on the base of LaAl, LiAl, LiLaAl, $LaAl_{oxid}$, $LiAl_{oxid}$, $LiLaAl_{oxid}$ allows to suggest it for making of electrodes accumulating hydrogen.

References

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