Microhardness of the amorphous and nanostructured alloys system $Al_{87}(Y, Gd)_5Ni_8$ as electrodes for hydrogen evolution

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It was investigated the processes of hydrogen evolution on aluminum amorphous and nanostructured electrodes $Al_{87}Y_5Ni_8$, $Al_{87}Y_4Gd_1Ni_8$, $Al_{87}Gd_5Ni_8$ in 1 M KOH alkaline solution. By electron microscopy method it was analysed the electrodes surface and found elemental composition before and after hydrogen evolution reaction in alkaline environment. It was also explored mechanical properties of AMA-electrodes before and after hydrogen evolution reaction. The main purpose of the research work was to find new electrode materials for hydrogen power engineering.

Keywords: amorphous metallic alloys, nanocrystals, microhardness, hydrogen evolution reactions

Introduction

The properties of the amorphous metallic alloys (AMA) are determined by the nature of the base metal, as well as the composition of alloying additions. Therefore, changing the elemental composition of the AMA it could be expanded the field of their applicability. The amorphous metallic alloys based on aluminum and alloyed with transition and rare-earth metals (RE) can demostrate catalytic action in various oxidation-reduction processes, including the hydrogen evolution reactions, while maintaining a high level of corrosion [1, 2]. The purpose of the research work was to investige electrochemical hydrogen evolution reactions from alkaline solutions by the Al-based amorphous alloys doped with Y and Gd.

Widely researched scientific problem – the hydrogen synthesis and accumulation by AMA alloys. Electrochemical hydrogen synthesis can be adjusted by changing the electrode composition, electrolyte concentration, temperature change of the electrochemical system [3, 4]. Promised for hydrogen evolution reactions are high resisted in aggressive environment amorphous metallic alloys, so they can be used as hydrogen allocation electrodes in corrosive solutions in wide range of pH. An important direction is the hydrogen accumulation, which takes place on the cathode in case of metallic hydrides formation [5].

The AMA are corrosion resistant in media with pH close to neutral, but electrodes based on Al are dissolving in strong alkaline and acidic aqueous solutions resulting in hydrogen evolution reactions [3-4]:

$$2Al + 6H_2O + 6OH^- = 3H_2 + 2[Al(OH)_6]^{3-}$$

$$2Al + 6OH_3^+ + 6H_2O = 3H_2 + 2[Al(OH_2)_6]^{3+}.$$

The homogeneous structure of the surface of amorphous alloys contributes to the formation of non-defective protective films and, thus, causes a high chemical resistance [6].

Experimental details

We investigated the chemical activity of amorphous metallic alloys based on Al: $Al_{87}Y_5Ni_8$, $Al_{87}Y_4Gd_1Ni_8$, $Al_{87}Gd_5Ni_8$. The electrodes were obtained by rapid hardening of the melt on the surface of copper drum rotating at high speed (10^6 K/sec). The electrochemical investigations were carried out in 1 M KOH aqueous solution. The AMAs were obtained at the G.V. Kurdyumov Institute for Metal Physics of the Ukrainian National Academy of Science (Kyiv).

The AMA was investigated using differential scanning calorimetry (DSC) with a heating rate of 10 K/min at the Silesian University Institute of Materials Science with the use of Perkin-Elmer Pyris 1. It is known [7] that in the temperature range of the first DSC maximum, the nanoscale AMA is carried out. From the DSC curves, the temperature of origin (T_1), growth (T_2) and the formation of α-Al (T_3) nanocrystals were determined [8].

Table 1 Temperatures (T ± 5K) of phase transitions of Al-based amorphous alloys

AMA	T_1, K	T_2, K	T_3, K
$Al_{87}Y_5Ni_8$	491	501	532
$Al_{87}Y_4Gd_1Ni_8$	441	456	503
$Al_{87}Gd_5Ni_8$	458	474	510

Thermal treatment of AMA in an oxygen-enriched medium with a heating rate of 10 °K/min to predetermined temperatures was carried out. For the electrochemical hydrogen evolution investigations of amorphous metallic electrodes we used three-electrodes scheme: AMA-electrode|1 M aqueous KOH|Ag/AgCI/KCl. For the attainment of the hydrogen release in thermostate cell at 293± 1°K during 30 min we used stationary potential E = -1,2 V and Jaissle Potentiostat/Galvanostat IMP 88PC-R.

The microhardness of AMAs was investigated by Vickers' method on the PMT-3 device before and after the hydrogen evolution reaction on aluminum amorphous and nanostructured alloys. The morphology of AMA surface was studied by the scanning electron microscopy. The microphotographs of the surfaces of the amorphous strips were taken by a scanning electron microscope REMMA-102-02 [9].

Results and discussion

Amorphous and nanostructured electrodes $Al_{87}Y_5Ni_8$, $Al_{87}Y_4Gd_1Ni_8$, $Al_{87}Gd_5Ni_8$ were investigated by the voltammetric method in the potentiodynamic mode. It was established the potential of hydrogen release E = -1.2 V, which is independent from the composition of the AMA-electrode.

From the dependence of the current density from time at E = -1.2 V, the volume of hydrogen released by the AMA electrodes in the 1 M KOH solution was calculated (Table 2). From table 2 it is seen that the largest volume of released hydrogen was on the AMA-electrode doped by Y and Gd.

Table 2 Microhardness of Al-based amorphous alloys before and after the hydrogen evolution reaction in alkaline environment.

AMA	Heat treatment	V_{H2}, mL/cm^2·min	H_{v1}, GPa	H_{v2}, GPa
$Al_{87}Y_5Ni_8$	–	0,39	3,52	3,12
	T_1	0,55	3,83	3,3
	T_2	0,35	3,65	3,41
	T_3	1,02	3,88	3,6
$Al_{87}Y_4Gd_1Ni_8$	–	0,65	3,23	1,81
	T_1	1,17	2,46	1,58
	T_2	0,97	2,66	1,73
	T_3	0,7	2,97	1,92

$Al_{87}Gd_5Ni_8$	–	0,22	3,27	2,58
	T_1	0,82	3,42	2,18
	T_2	0,37	3,87	1,95
	T_3	*	3,93	*

H_{v1} – microhardness before the hydrogen evolution reaction;

H_{v2} – microhardness after the hydrogen evolution reaction;

* – the sample couldn't stand the conditions of the experiment.

An important characteristic of the AMA-electrodes in electrochemical hydrogen evolution reactions is the resistance to hydrogen overstress [10]. That's why it was necessary to investigate the microhardness of amorphous and nanostructured alloys before and after use them as H_2-electrodes. Results of microhardness measurements are given in Table 2. The highest microhardness have alloys dopped only by Y or Gd. Microhardness due to annealing increases. At T_3 which corresponds to the total formation of nanocrystals, increases to 3.9±0.5 GPa. This is due to the fact that after the first stage of crystallization Al nanocrystals are formed. X-ray structural analysis of samples showed that in all cases the Al lattice period is higher than in pure Al (0.40494 nm), which may indicate the formation of a solid Al(R) solution [8]. Based on the X-ray data obtained, the size of the Al(R) crystals after the heat treatment at T_3 was calculated by the Hall method [11]. The results of such calculations are presented in Table 3.

The crystallite sizes calculated from the X-ray diffraction analysis are close to those obtained by electron microscopy (Table 3).

Table 3 Temperature of annealing (T_3) and averaged diameter (D) selected Al nanocrystals after the first stage of AMA crystallization.

№	AMA	$T_{annealing} \pm 1$, K	D, nm
1	$Al_{87}Y_5Ni_8$	532	20 ± 4
2	$Al_{87}Y_4Gd_1Ni_8$	503	9 ± 2
3	$Al_{87}Gd_5Ni_8$	510	15 ± 3

The results of electron microscopy of the $Al_{87}Y_4Gd_1Ni_8$ alloy are shown on Fig. 1. The microphotography proofs the amorphous state of the inial alloys. There are dark grains of Al(R), the light and gray regions of the amorphous matrix, which may be due to the different distribution of REM and Ni within it. This is evidence of the structuring of amorphous matrix after initial crystallization of Al(R).

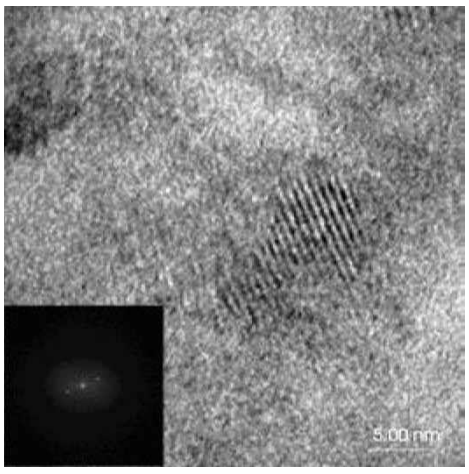
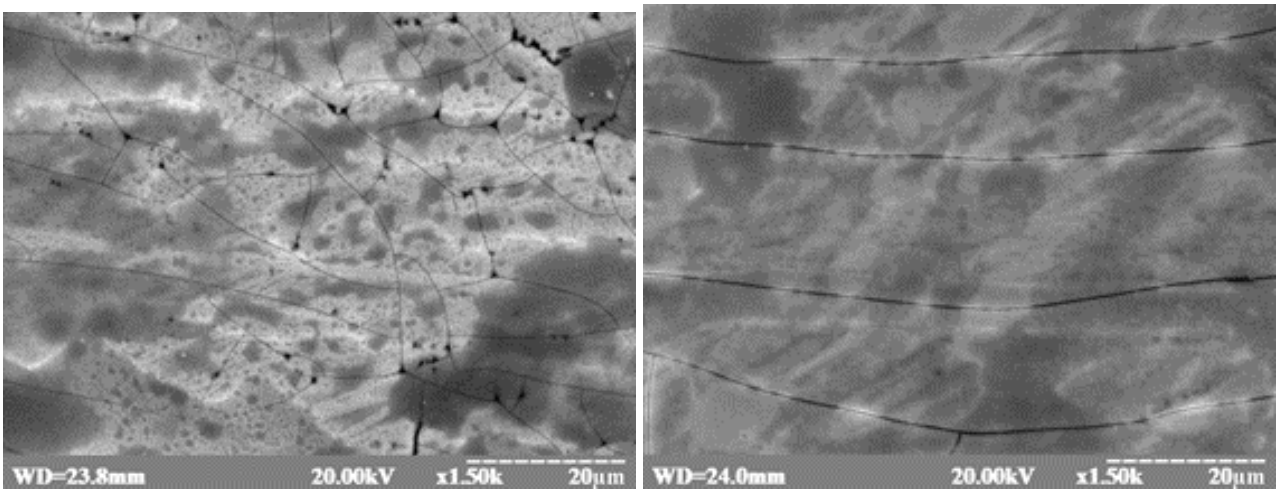


Fig. 1 Microstructure of $Al_{87}Y_4Gd_1Ni_8$ AMA annealed at 503 K [8].

The size of Al(Y) or Al(Gd) nanocrystals of 15 and 20 nm leads to an increasing of microhardness. The simultaneous presence of Y and Gd inhibits the growth of nanocrystals to a size of 9 nm, which leads to an increasing of the free volume in the amorphous matrix and to microhardness decreasing.

AMA electrodes were investigated by scanning electron microscopy [9]. From the SEM photos it could be seen that the surface of the alloys becomes fragile after the processes of hydrogen evolution. Cracking degree depends on the elemental composition of the samples. Partial replacement of yttrium on gadolinium leads to an increasing in the stability of the electrodes to mechanical cracking. Similar results are described in [10].



a b

Fig. 2 SEM photos of the annealed (T_3) surface and after using AMA electrodes $Al_{87}Y_5Ni_8$ (a) and $Al_{87}Y_4Gd_1Ni_8$ (b) in the electrochemical hydrogen evolution reaction during 30 min in the 1 M KOH aqueous solution.

Investigation of microhardness of the AMA electrodes after an electrochemical reaction indicates a decrease in their mechanical strength. This is due to the dissolution of Al from the surface of the electrodes [10], both before and after heat treatment. The elemental composition of aluminum amorphous alloys before and after annealing at temperatures T_1, T_2, T_3 and subsequent hydrogen evolution during 30 minutes from 1 M KOH solution is presented in Table. 4. The results of the AMA surface investigation by the X-ray energy-dispersive spectroscopy showed that the content of Y, Gd and Ni increaseds on the surface (Table 4).

Table 4 Elemental composition of the AMA electrodes annealed and used in the electrochemical hydrogen evolution reaction (30 min), E=-1,2 V in 1M KOH

AMA	Heat treatment	V_{H2}, mL/cm^2·min	Elemental composition, at %			
			Al	Y	Gd	Ni
$Al_{87}Y_5Ni_8$	–	0,39	14, 77	12,99	—	24,75
	T_1	0,55	19,58	12,45	—	22,20
	T_2	0,35	43,39	9,84	—	21,80
	T_3	1,02	26,80	12,24	—	34,17

$Al_{87}Y_4Gd_1Ni_8$	–	0,65	24,02	11,54	16,26	13,09
	T_1	1,17	11,93	13,53	3,60	44,17
	T_2	0,97	19,28	11,08	3,37	38,04
	T_3	0,7	13,81	11,73	3,31	22,98
$Al_{87}Gd_5Ni_8$	–	0,22	20,28	—	16,14	24,19
	T_1	0,82	21,72	—	14,68	22,44
	T_2	0,37	23,87	—	14,11	30,52
	T_3	*	*	*	*	*

* – the sample couldn't stand the conditions of the experiment

From the microphotographs it could be seen (Fig. 2) the two colored zones which were formed on the surface. Alloying only by yttrium creates finely dispersed areas on the surface of the AMA electrodes. The combined alloying by Y and Gd results in the formation of long dark-colored regions enriched with Ni atoms.

Conclusion

Analyzing the research results, it can be seen that the $Al_{87}Y_5Ni_8$ alloy during heat treatment at the temperature T_3 (stable nanocrystallization) produces a sufficiently large amount of hydrogen - 1.02 mL/cm^2·min and has the highest microhardness of 3.6 GPa. The $Al_{87}Y_4Gd_1Ni_8$ alloy at the T_1 temperature (nanocrystals origin) produces the largest amount of hydrogen - 1.17 mL/cm^2·min among the investigated samples, however, its microhardness is 1.58 GPa much less than in case of the $Al_{87}Y_5Ni_8$ alloy.

By the method of electron microscopy it was shown that due to the electrochemical hydrogen evolution reaction from the 1 M KOH solution, an overstress of the surface of aluminum amorphous alloys is observed. It was established that on the surface of the electrodes the amount of Y, Gd and Ni increases as a result of dissolving Al in an alkaline solution. The volume of released hydrogen increases with an increase of Ni content during aluminum dissolution from the surface of AMA electrodes.

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