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STUDY OF THE INFLUENCE OF γ-RADIATION ON THE ELECTROCATALYTIC ACTIVITY OF BINARY AND TRINARY NICKEL-BASED ALLOYS

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Abstract: Currently, the synthesis of electrodes with catalytic activity in the water-splitting reaction and the enhancement of their electrocatalytic properties are crucial for hydrogen production via electrolysis. The generation of radiation defects on electrode surfaces due to ionizing radiation and assessing their impact on the catalytic activity of synthesized electrodes in hydrogen production by electrolysis of water is a significant scientific challenge.

This study examines the effect of γ-radiation on the catalytic activity of binary (Ni-Mo) and ternary alloys (Ni-Mo-P), obtained using the electrochemical method from alkaline and alkali-citrate electrolytes. The alloys were analyzed before and after annealing in an air atmosphere at 773 K for one hour. It was found that under the influence of γ-radiation, the catalytic activity in the hydrogen evolution reaction in a neutral environment (0.5 M Na_2SO_4) increases by 12.2% for annealed Ni-Mo binary thin films, whereas the activity of non-annealed samples remains largely unchanged. For Ni-Mo-P ternary alloys, the catalytic activity decreases by 28.16% after annealing and γ-radiation exposure. This behavior of the catalysts is explained by changes in the crystal lattice of the resulting films under the influence of γ-radiation.

Keywords: nickel, molybdenum, phosphor, polarization, γ-ray.

1. Introduction

In the modern world, with an acute shortage of fossil energy and resources, obtaining hydrogen as a "clean" energy carrier directly from renewable sources by decomposing water is particularly important. Noble metals are known to be the most active materials for the hydrogen evolution reaction (HER), but their high cost prohibits their widespread industrial use for hydrogen production. Only 4% of hydrogen gas is produced from water electrolysis, primarily due to the high cost of noble metal catalysts. To achieve more economical hydrogen production via electrolysis, it is imperative to develop new electrode materials with enhanced electrocatalytic activity. Hydrogen evolution during water electrolysis (HER) is one of the most frequently studied reactions. The HER process is relatively straightforward, involving a limited number of steps with a single intermediate. The kinetics and mechanism of the HER on Ni-containing alloys obtained by electrodeposition have been the focus of numerous studies [1-3]. Research has demonstrated that the increased activity of electrodes obtained by electrodeposition is mainly due to the increased surface area, often neglecting possible synergistic effects [3]. However, in the production of nickel alloys by thermal decomposition, suitable precursors with obvious synergistic effects have been obtained. Among pure metals, precious metals remain the best catalysts for HER, but their high cost and susceptibility to surface poisoning during

electrolysis limit their industrial application.

The selection of an electrolyte for the electrochemical synthesis of electrodes for the water-splitting reaction and the enhancement of their electrocatalytic properties are crucial for hydrogen production via electrolysis. Currently, the generation of radiation defects on electrode surfaces when exposed to ionizing radiation and elucidating their role in hydrogen production during water electrolysis is a pressing scientific challenge. Basically, studies on ionizing radiation have primarily focused on damage to organic materials [4-6], with insufficient exploration of the effects of γ-radiation on inorganic compounds and alloys. The earliest study of γ-ray damage in macromolecular crystallography (MX) was published in 1962 [7], and since then, efforts have been made to comprehend the physical and chemical phenomena underlying the observed damage and the rate at which these processes occur.

Alloys under irradiation are nonequilibrium systems, developing concentration gradients in point defects and complexes formed during irradiation. Concentration gradients cause atomic flows that disrupt thermodynamic equilibrium, where the chemical potential of each species remains constant throughout the system. Such fluxes result in segregation and restructuring of the alloy, leading to the formation of new phases and changes in both short-range and long-range order. Radiation flux has multifaceted effects on materials, such as increasing the concentration of point defects and altering the composition near sinks, a phenomenon known as radiation segregation [8]. Exposure to radiation, such as in a nuclear power plant, can induce changes in the atomic structure of minerals, which subsequently affects their physical and chemical properties. It is known that irradiation has minimal impact on the atomic structure and properties of Ca and Mg carbonates. This insensitivity to radiation is due to the predominantly ionic nature of the interatomic bonds in them, which can relax and restore their original configuration, thereby minimizing damage and irreversible changes after radiation exposure [9]. A critical issue affecting the structural integrity of irradiated materials is radiation-enhanced diffusion due to the formation of vacancies, interstices, and point defects. These defects typically degrade the mechanical and thermal properties of alloys [10,11]. Experimental studies, such as those by the authors of [12], have sought to understand changes in material properties upon irradiation, including microstructural changes, cracking, and hydrogen embrittlement. However, these tests are complex and costly due to the requirements for controlled irradiation, sample preparation, and post-irradiation property assessments [13]. Computer modeling provides an alternative tool for studying the effects of irradiation on structural integrity and changes in material properties due to irradiation. These simulations provide valuable insights into the behavior of alloys under irradiation [14,15].

In this work, we investigated the effect of γ-radiation on the electrocatalytic activity of Ni-Mo and Ni-Mo-P alloys, both with and without heat treatment, during the electrolysis of water in a neutral (0.5M Na_2SO_4) environment.

2. Research Methodology

Ni-Mo thin films were obtained from alkaline solutions containing $NiSO_4$ – 0.19 M, Na_2MoO_4 – 0.21 M, $NiCl_2$ – 0.06 M, H_3BO_3 – 0.1 M, NH_4OH – 7 M at pH = 11.2, with a current density (i_c) of 20 mA/ cm^2 and a temperature of T = 298 K [16]. For the preparation of the Ni-Mo-P ternary alloy, 0.2 M sodium pyrophosphate ($Na_4P_2O_7$) was introduced into the alkaline Ni-Mo deposition electrolyte. Additionally, the electrolyte underwent some changes; the pH value was reduced to 9 by adding sodium citrate to the electrolyte. The catalytic activity of samples was studied both immediately after electrolysis and after heat treatment at 773 K in an air atmosphere for one hour. All four samples were obtained on nickel substrates. Before and after

heat treatment, they were exposed to γ-radiation from ^{60}Co with a dose of 968 kGy, at a dose rate of 160 Gy/sec.

3. The discussion of the results

To determine the effect of irradiation on the catalytic activity of the obtained samples, thin Ni-Mo films were exposed to γ-radiation before and after heat treatment. The deposited thin Ni-Mo films, obtained by electrolysis, contained 73.5% Ni and 13.3% Mo [16,17]. The catalytic activity of films, both annealed and unannealed was measured before and after exposure to (0.5 M Na_2SO_4) γ-radiation, using the slope of Tafel curves.

Figure 1 shows the polarization curves of the catalytic activity of Ni-Mo thin films in a neutral environment for samples before and after annealing (Figure 1a, b), and the same samples before and after exposure to γ-radiation (Figure 1c, d). Based on these curves, to determine the catalytic activity of the catalysts under study, curves were constructed in lgi-E coordinates for Ni-Mo electrodes.

The slope of the Tafel curves (tgα) indicated that the catalytic activity of samples not subjected to heat treatment remains almost unchanged after exposure to γ-radiation, whereas the catalytic activity of samples subjected to heat treatment increases by approximately 12.2%.

Introducing phosphorus into the Ni-Mo binary alloy, even in small quantities (1.06%), results in a 14.5% increase in the catalytic activity of the Ni-Mo electrode and a 38.47% increase in corrosion resistance. It is noteworthy that Ni-Mo alloys with a Mo content of 64.85% also exhibited high corrosion resistance.

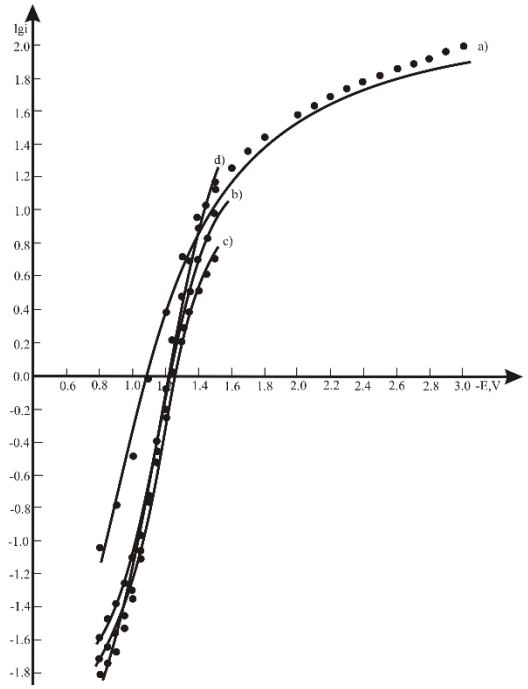

Fig. 1. Effect of γ-radiation on the catalytic activity of Ni – Mo alloys. a - sample not subjected to annealing and γ-radiation exposure, b - sample subjected to annealing, c - sample subjected to annealing and γ-radiation and d - sample not exposed only to γ-radiation.

It should be noted that increasing the molybdenum content in the alloy composition also led to a nearly twofold decrease in catalytic activity. In the case of doping nickel-molybdenum alloys with phosphorus, both the catalytic activity of the alloys and their corrosion resistance

increase.

Figure 2 shows the polarization curves of the electrolysis of water in a neutral environment on a nickel electrode coated with Ni-Mo-P, where the phosphorus content ranged from 0.9% to 1.2%. In this case, also based on Figure 2, curves were plotted in lgi-E coordinates, and tgα values were calculated from the slopes of the curves. When studying Ni-Mo-P ternary alloys, a completely different picture is observed.

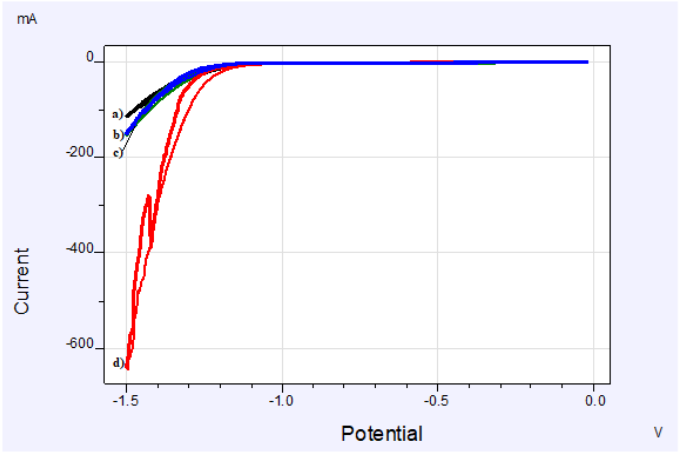

Fig. 2. Effect of γ radiation on the catalytic activity of Ni–Mo-P alloys. a - sample subjected to annealing and exposure to γ-radiation, b - sample not subjected to annealing, exposed to γ radiation, c - sample annealed without γ-radiation, and d - sample not subjected to either annealing or irradiation.

The best catalytic properties were exhibited by Ni-Mo-P samples that were not subjected to annealing and γ-radiation. The catalytic activity of other Ni-Mo-P samples is approximately the same; these are samples subjected to annealing and irradiation.

Comparative studies were carried out on the catalytic activity of not only the synthesized samples but also the electrocatalytic activity of the electrodes most commonly used in HER reactions, these include electrodes made of Ni, Pt, and steel. The table shows comparative data on the catalytic activity of all studied electrodes.

Table

The comparative catalytic activity of synthesized Ni-Mo, Ni-Mo-P electrodes, and electrodes traditionally used in water-splitting reactions

No.	Electrode		tg α (mV)
1.	Ni-Mo	before annealing	105
		after annealing	123
		before annealing after exposure	110
		after annealing and exposure	108
2.	Ni-Mo-P	before annealing	89.8
		after annealing	129
		before annealing after exposure	132.3
		after annealing and exposure	135
3.	Pt		140
4.	Ni		159
5.	Steel -3		192

The data presented in the table allow us to conclude that the introduction of a small amount of phosphorus into the composition of thin films increases the catalytic activity of Ni-Mo by 14.5%. Irradiation leads to an increase in the catalytic activity of Ni-Mo thin films subject to annealing, while the activity of electrodes not subject to annealing has almost no effect. Such changes in the catalytic activity of alloys after irradiation can be explained by changes in their crystal structure as a result of exposure to ν-radiation and the appearance of defects in their crystal lattice.

Some of the high-intensity radiation used for experiments is absorbed by the crystals, forming free radicals, which can cause radiation damage even at cryotemperatures (~100 K), potentially leading to incorrect conclusions when studying their structure and properties [18]. The interaction of intense synchrotron radiation with molecular crystals often modifies the crystal structure by breaking bonds, forming fragments, and hence causing disorder [19]. There is also an opinion that a) irradiation (with X-ray beams, gamma rays, and electrons) of metals and alloys with a dose of less than 10^5 J/kg, and semiconductor crystals with a dose of less than 10^3 J/kg does not lead to additional defect accumulation. However, it leads to defect elimination and transition of the crystal to a more equilibrium state; b) ionization processes play a crucial role in restructuring defects in crystals with both semiconductor and metallic conductivity. The restructuring of the crystal occurs as a result of the energy stored in the crystal, which is released due to chain reactions of defect annihilation initiated by ionization. The transition of the crystal to an equilibrium state is accompanied by improvements in its physical properties [20]. Radiation exposure results in elongation and rupture of disulfide bonds, decarboxylation of side chains of aspartic and glutamic acids, disordering of methionine sulfur, and photoreduction of metal centers [21-24].

The formation of defects in the crystal structure of alloys not only increases the actual surface area of the films but also creates new active points on the electrode surface, thereby enhancing their electrocatalytic activity. Thus, we can conclude that radiation effects on alloys have different effects on their properties. In binary Ni-Mo alloys, annealing reduces catalytic activity, while radiation exposure increases it; in ternary Ni-Mo-P alloys, the introduction of phosphorus into the binary Ni-Mo alloy increases the catalytic activity of the catalyst, but annealing and γ-radiation exposure decrease it.

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ИССЛЕДОВАНИЕ ВЛИЯНИЯ γ-ИЗЛУЧЕНИЯ НА ЭЛЕКТРОКАТАЛИТИЧЕСКУЮ АКТИВНОСТЬ ДВОЙНЫХ И ТРОЙНЫХ СПЛАВОВ НА ОСНОВЕ НИКЕЛЯ

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Резюме: В настоящее время ощущается острая нехватка ископаемой энергии и ресурсов, поэтому получение водорода как «чистого» носителя энергии непосредственно из возобновляемых источников путем разложения воды является особенно важным. Синтез электродов, обладающих каталитической активностью в реакции разложения воды и исследования по улучшению их электрокаталитических свойств относятся к основным направлениям получения водорода методом электролиза. Генерация радиационных дефектов на поверхности электродов под воздействием ионизирующих излучений и определение их влияния на каталитическую активность синтезированных электродов при получении водорода электролизом воды является актуальной научной задачей.

В работе исследовано влияние действия γ-излучения на каталитическую активность двойных (Ni-Mo) и тройных сплавов (Ni-Mo-P), полученные электрохимическим методом из щелочного и щелочно-цитратного электролитов. Исследованию были подвергнуты сплавы до и после отжига в атмосфере воздуха при температуре 773К в течении часа. Установлено, что под действием γ-излучения каталитическая активность в реакции выделения водорода в нейтральной среде (0.5 M Na_2SO_4) двойных тонких пленок Ni-Mo после отжига повышается на 12.2%, тогда как активность образцов не подвергнутых отжигу почти не меняется. В случае же с тройными сплавами Ni-Mo-P каталитическая активность образцов после отжига и действия γ-излучения уменьшается на 28.16%. Такое поведение катализаторов объясняется изменениями в кристаллической решетке полученных пленок под воздействием γ-излучения.

Ключевые слова: никель, молибден, люминофор, поляризация, γ-лучи.

NİKEL ƏSASLI BİNAR VƏ ÜÇLÜ ƏRİNTİLƏRİN ELEKTROKATALİTİK AKTİVLİYİNƏ γ-ŞÜALARININ TƏSİRİNİN ÖYRƏNİLMƏSİ

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Xülasə: Hazırda fosil enerji və resursların kəskin çatışmazlığı var, ona görə də suyun parçalanması yolu ilə hidrogenin "təmiz" enerji daşıyıcısı kimi birbaşa bərpa olunan enerji mənbələrindən əldə edilməsi xüsusilə vacibdir. Suyun parçalanması reaksiyasında katalitik aktivliyə malik elektrodların sintezi və onların elektrokatalitik xüsusiyyətlərini yaxşılaşdırmaq üçün tədqiqatlar elektroliz yolu ilə hidrogenin alınmasının əsas istiqamətlərindəndir. İonlaşdırıcı şüaların təsiri altında elektrodların səthində radiasiya defektlərinin yaranması və suyun elektrolizi yolu ilə hidrogen istehsalında sintez edilmiş elektrodların katalitik aktivliyinə təsirinin müəyyən edilməsi aktual elmi problemdir.

Bu işdə qələvi və qələvi-sitrat elektrolitlərindən elektrokimyəvi üsulla alınmış ikili (Ni-Mo) və üçlü ərintilərin (Ni-Mo-P) katalitik aktivliyinə γ-şüalanmanın təsiri tədqiq edilmişdir. Ərintilər bir saat ərzində 773 K temperaturda hava atmosferində termiki emaldan əvvəl və sonra tədqiq edilmişdir. Müəyyən edilmişdir ki, γ-şüalanmanın təsiri altında ikiqat Ni-Mo nazik təbəqələrinin neytral mühitdə (0.5 M Na_2SO_4) termiki emal edildikdən sonra hidrogenin ayrılması reaksiyasında katalitik aktivliyi 12.2% artır, termiki emala məruz qalmayan nümunələrin aktivliyi isə demək olar ki, dəyişmir. Ni-Mo-P üçlü ərintiləri termiki emal və γ-şüalanmadan sonra nümunələrin katalitik aktivliyi 28.16% azalır. Katalizatorların bu davranışı γ-şüalanmanın təsiri altında əmələ gələn təbəqələrin kristal qəfəslərinin dəyişməsi ilə izah olunur.

Açar sözlər: nikel, molibden, fosfor, polyarizasiya, γ-şüaları.