



Full Length Article

Corrosion behavior of magnesium in aqueous sulfate-containing electrolytes

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Abstract

Studies have been conducted on the corrosive behavior of magnesium in aqueous sulfate electrolytes (0.5 mol/L MgSO_4 ; 0.5 mol/L Na_2SO_4 ; 0.5 mol/L MgSO_4 + 0.5 mol/L Na_2SO_4).

The composition structure and morphology of the surface of the samples were studied using scanning electron microscopy in combination with X-ray spectral microanalysis. The results of the experiments showed the formation of a surface film inhomogeneous in its structure and composition with the main components $\text{Mg}(\text{OH})_2$ and MgO . An increase in the exposure time of the electrode in solution led to the formation of microcracks on the main film caused by internal stress because of hydration of magnesium oxide produced during corrosion. The salt composition of the electrolyte determines the morphology and thickness of corrosion films due to differences in the solubility of the products formed during the hydrolysis of magnesium oxide and the kinetics of this process.

Applying the methods of scanning electron microscopy X-ray electron analysis gravimetry and voltammetry it has been established that at various stages of magnesium corrosion in different electrolytes the growth rates of corrosion films are determined by the kinetics of magnesium oxide formation its hydration and dissolution followed by crystallization in the form of a brucite phase of loose sediments on the surface.

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1. Introduction

Magnesium is a promising anode material for chemical power sources (CPS) and has some advantages in aqueous solutions compared to traditionally used metals, including a higher negative electrode potential (−2.37 V vs. standard hydrogen electrode (SHE)) and high specific theoretical capacity (2202 mA h/g) [1,2]. With all this, magnesium is not cor-

rosion resistant in aqueous electrolytes [3–5]. Therefore, the use of this material for power converters is unlikely, unless the problem of magnesium corrosion is effectively addressed.

Despite the fact that many works are usually devoted to the study of the structure of the formed film after corrosion [6] in this work we study the stages of the corrosion process and the transition to different structures.

In the atmosphere of dry air, a layer of a gray film of magnesium oxide with a thickness of 20–50 nm [7] is formed on the surface of magnesium. In humid air and aqueous solutions, as a result of electrochemical processes, a film is formed on magnesium consisting of hydrated magnesium oxide (50%–60% $\text{Mg}(\text{OH})_2$) [8]. After immersing the electrode in the solution it is coated with a film having a two-

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layer structure: an inner layer of MgO and an outer layer of Mg(OH)₂ [9]. In neutral and alkaline solutions magnesium undergoes local corrosion according to studies [6,10].

The outer layer has a very porous and relatively loose structure, while the inner layer is less porous or better protects the metal from dissolution. Over time, cracks begin to form on the film. It is generally known that MgO and Mg(OH)₂ are poor ion-conductors, however, polarization current can easily pass through pores in film cracks. Growth of the outer layer is possible due to migration and combination of Mg²⁺ and OH[−] in the outer layer and also deposition of Mg²⁺ and OH[−] from the solution on the film surface [11]. During this electrochemical process, 2 electrons are produced. However, there are hypotheses that this process should include single-electron transitions that have not been defined yet. On the outer part of the surface layer, as in the pores of the surface film, the deposition of Mg(OH)₂ by reactions (1) and (2) is considered as an external process [11].



Meanwhile, the conversion occurs mainly between the inner and outer layers inside the film (3):



Anodic magnesium polarization facilitates the formation of MgO at the film/Mg interface. As a consequence of this, the thickened inwardly growing MgO layer will crack more severely due to internal pressure, i.e., a smaller volume of MgO than magnesium metal [12–15].

A large number of research works confirm the presence of cracks, pores or breaks on the surface film during magnesium corrosion [16]. According to the assumption made in 1997, in these regions anode and cathode partial reactions are regulated by Tafel kinetics [5]. Thus, during magnesium corrosion, cathode (white) and anode (dark) regions are observed on the surface. The dark area on the surface of magnesium during corrosion was first discovered by Song who proved that the appearance of a dark region on the surface of the film is associated with the active dissolution of the metal and the evolution of hydrogen [5,17–20]. In the dark areas, the evolution of hydrogen was abundant, but in the white areas there was a insignificant evolution of hydrogen. The evolution of active hydrogen passed from one area to another along with the destruction of the film in the dark region. This corrosion, accompanied by the copious evolution of hydrogen, was not similar to a typical corrosion process. Such an anomalous phenomenon is called the "negative differential effect" (NDE), where the rate of hydrogen evolution per magnesium increases with its anodic dissolution [21]. There are several points of view explaining the reason of this abnormal effect [22–24]: partial film theory, magnesium hydride theory [24], metal inter-granular destruction theory [25], metal self-destruction [26], staged anode reactions (partial film formed

by a monovalent magnesium ion) [5,27–29] and the theory of cathodic catalytic activity [30].

The film theory explains this by the partial destruction of the protective film on the surface of magnesium during anodic dissolution. The electrolyte enters through the slits in the film, which interacts with the metal and this leads to intense hydrogen evolution. However, some authors [5,25] believe that the anomalous dissolution of magnesium is caused by an increase in the intensity of metal self-dissolution as a result of the growth of active sites due to the falling off of small metal particles from the surface. With an increase in the anode current, the process of particle chipping intensifies; accordingly, the rate of the process of self-dissolution of magnesium increases, which leads to an increase in the volume of released hydrogen.

"Partial film mechanism formed by Mg⁺" or staged anodic reactions suggests that enhanced hydrogen evolution due to anodic polarization is the result of the chemical reaction of Mg⁺ with water indicated in the reaction (5). Anode hydrogen evolution (AHE) is accelerated due to a positively shifted polarization potential or current density because of an increase in the amount of the Mg⁺ ion formed from the electrochemical reaction (4) [30,31]. Following this theory, monovalent magnesium is formed in the first stage by the reaction:



The formed Mg⁺ ion is an intermediate active particle that enters into a chemical reaction as a result of which hydrogen is evolved [11]:



The evidence that the calculated valence of experimentally dissolved magnesium metal ranged from 1.33 to 1.66 is given in [32]. It can be assumed that Mg⁺ reacts with water within milliseconds [33]. According to the well-known theory of quantum mechanics, the simultaneous transfer of two electrons in one step is prohibited, and the transition of one electron is simpler than the transfer of 2 electrons. However, at present, there is no accurate experimental data confirming the existence of monovalent magnesium ion in solutions. Nevertheless, during gas phase studies, the short-term presence of Mg⁺ ion was confirmed in work [34], as well as the coating of the metal surface with a film during corrosion. In accordance with the theory of the staged course of the anodic reaction, the Mg⁺ ion briefly appears on the surface of metallic magnesium in regions free from the film. In addition, there is scientific version about the existence of Mg⁺ even in the form of Mg·Mg²⁺. However, Mg·Mg²⁺ is thermodynamically unstable and its existence at any time is not possible. Some scientists [35] suggested that the dark flakes of the corrosion product separating from magnesium could be Mg(OH)₂ containing tiny particles of magnesium. The dark surface film may be a mixture of Mg⁺ and MgO/Mg(OH)₂ films.

According to the theory of magnesium hydride, metallic magnesium is electrochemically or chemically reduced to a

hydride and chemically reacts with water with the release of hydrogen. Magnesium hydride can be determined by X-ray phase analysis. However, with a stronger anodic polarization, the formation of MgH_2 is more difficult, consequently, this theory is not able to interpret the NDE [18].

According to the mechanism of increased cathodic catalytic activity of the univalent ion, Mg^+ cannot participate in hydrogen evolution and suggests that the enhanced hydrogen evolution due to anodic polarization is the result of a normal cathodic reaction (i.e., NCR) catalyzed by the catalyst [36]. It is also supposed that Mg^+ can diffuse through the film with porous $\text{MgO}/\text{Mg}(\text{OH})_2$ forming corrosion products, in the region where both anodic hydrogen evolution and magnesium dissolution occur. There is an assumption that in these areas, magnesium hydroxide re-crystallizes from the amorphous phase to the crystalline phase with the formation of brucite. Hence, the identification of the mechanisms of hydrogen evolution is one of the most important points for determining the model of the corrosion dissolution of magnesium. Hydrogen evolution behavior is also the most important parameter for evaluating the feasibility of any proposed NDE mechanisms.

According to our point of view, it would be more logical to assume the formation of a monovalent magnesium ion during anodic oxidation of the metal, and its subsequent oxidation to a more stable divalent ionic form.

Metal passivation and the phenomenon of negative differential effect do not allow realize the high energy potential of the magnesium anode. The value of the stationary potential of magnesium in aqueous solutions is between the values of the equilibrium potential of magnesium and hydrogen.

It can be reasonably considered generally accepted today that the electrochemical behavior of active metals in solutions depends on the nature of surface formations. Although the composition and structure of the surface film, as well as the ratio of its ionic and electronic conductivity determine the rate of metal corrosion, it is the composition of the solution that ultimately determines all these properties of corrosion films. Understanding the mechanism of the effect of the composition of the solution on the properties of corrosion films is of great theoretical importance and undoubtedly makes a great contribution to solving practical problems.

The purpose of this work is to study the stages of formation of a passivating film, its properties and influence on the electrochemical behavior of magnesium in sulfate-containing electrolytes with low corrosion aggressiveness towards magnesium compared to chloride electrolytes, and currently insufficiently studied.

2. Experimental part

The following salts were used to prepare solutions of various concentrations: magnesium sulfate 7-aqueous (99.5%) and sodium sulfate anhydrous (99.5%). Magnesium samples were kept in solutions of magnesium sulfate, sodium sulfate, and a mixed solution for 1, 5, 10, 20, and 30 min and at longer intervals of up to 1 month to form corrosion films on them for further research.

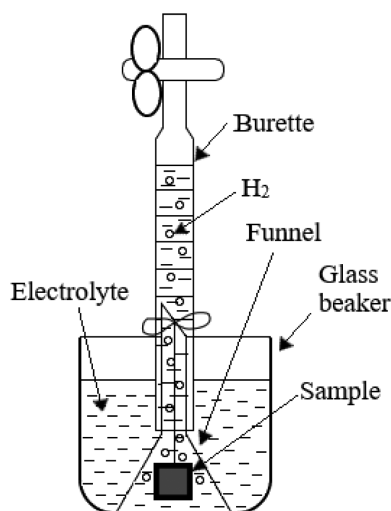


Fig. 1. Scheme of the installation for determining the volume of hydrogen by the volumetric method.

Electrochemical measurements of potential versus time were conducted at ambient temperature in sulfate solutions of various concentrations in a three-electrode electrochemical cell using AUTOLAB PGSTAT potentiostat-galvanostat (Netherlands). As the working electrode the end face of a magnesium rod (99.98%) with an area of 0.17 cm^2 was used. As the counter electrode a platinum plate with an area of 6.3 cm^2 and Ag/AgCl sat. KCl electrode was used as a reference electrode ($E=0.197 \text{ V}$ vs. the standard hydrogen electrode).

Gravimetric studies were carried out with magnesium samples $10 \text{ mm} \times 10 \text{ mm} \times 10 \text{ mm}$ in size, were cast on four sides with a cold curing metallurgical epoxy resin to isolate the metal from the electrolyte. The surface area exposed to the solution was 1 cm^2 . Exposure of magnesium in electrolytes was carried out in a three-necked flask under vacuum. The flask was purged with argon under constant stirring with a magnetic stirrer to remove carbonates from the solution.

Before each measurement, the magnesium electrode was machined with abrasive paper (grain size $5\text{--}7 \text{ }\mu\text{m}$) and degreased with ethyl alcohol. All experiments were carried out at a temperature of $25 \text{ }^\circ\text{C}$ with an accuracy of $\pm 0.1 \text{ }^\circ\text{C}$. Weighed samples of magnesium were immersed in the solution in nylon bags, which prevented corrosion products from falling out and mixing them in solution. After exposure, metallic magnesium was weighed with a bag for determining the mass of metal along with corrosive products. Then the mass of precipitated products was determined, as well as the mass of metal without corrosive deposits.

Volumetric researches were performed under conditions identical to gravimetric studies. The prepared sample was suspended vertically in the solution. The evolution of hydrogen was collected in a burette above the sample (Fig. 1).

All the measurements were performed three times, followed by statistical analysis on blunder and averaging of the result obtained.

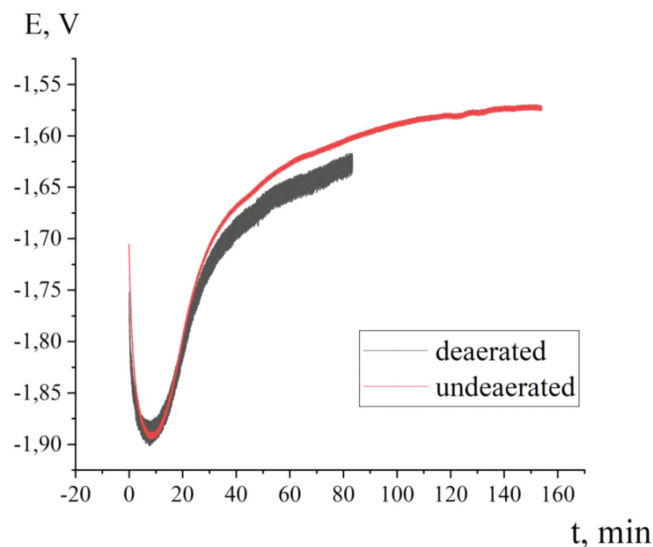


Fig. 2. Dependence of magnesium electrode potential on exposure time in 0.5 mol/L MgSO_4 electrolyte.

Micrographs of the magnesium electrode surface and surface film composition were obtained using a Quanta 200i 3D scanning electron microscope (FEI Company, USA). (Japan).

Samples were analyzed through a Cu K α radiation source with wavelengths of 1.5406 Å. Samples were scanned at a rate of 0.05 min⁻¹, starting at an angle of 10° and ending at an angle of 80°.

3. Results and discussion

3.1. The initial stage of corrosion

Previously, [37] we used electrochemical methods to correlate the contribution to the polarization resistance of the thicknesses of layers, which determine the complex structure of the film, in particular, of two main layers: the magnesium oxide layer and magnesium hydroxide layer. The research was mainly devoted to the polarization of the corroding electrode. The present study focuses on the composition of the corrosion film and the kinetics of the corrosion process.

The change in the potential of the corroding electrode has an unusual form and represents a curve with a minimum for sulfate systems in Fig. 2.

It is characteristic that the potential at the very beginning sharply shifts to the negative side, and then gradually passes to the drift in the positive side, reaching the station in about an hour. The course of the curve is quite reproducible, and the deviations do not exceed the measurement errors. Apparently, the process of potential change is determined by the interaction of magnesium with water, as evidenced by the insignificant difference in changes in the shape of the potential in de-aerated solutions and in solutions saturated with air that is containing oxygen, (Fig. 2). The contribution of oxygen to the corrosion process gets more perceptible upon reaching a plateau, when, as passivation progresses, the rate of water re-

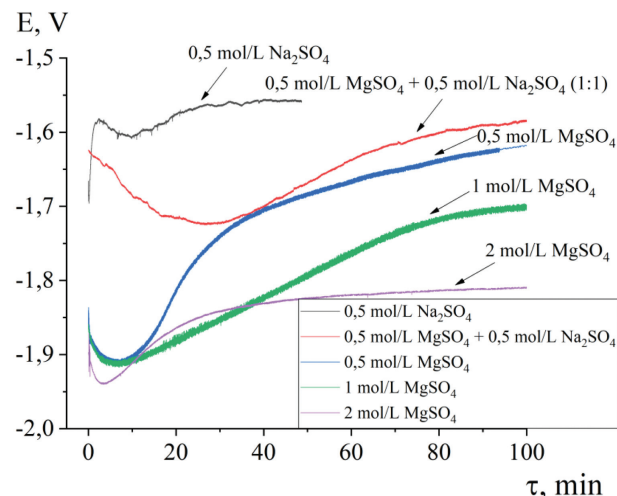


Fig. 3. Dependence of the magnesium electrode potential on the exposure time in different electrolytes.

duction slows down and the contribution of oxygen reduction becomes more noticeable for the aerated solution (Fig. 2).

Fig. 3 shows the curves of potential changes over a 100 min time interval for all the studied solutions (0.5 mol/L, 1 mol/L, and 2 mol/L magnesium sulfate, 0.5 mol/L sodium sulfate and a mixture of 0.5 mol/L sodium sulfate and 0.5 mol/L magnesium sulfate). During this time the system comes to a stationary state.

The general behavior of the curves is repeated with some peculiarities. As the MgSO_4 concentration increases a noticeable shift of the stationary state potential to the positive region occurs, while the initial potentials are close. Sodium sulfate also significantly shifts the potential in a negative direction compared to magnesium sulfate.

Since metal surfaces prepared in the air, are an oxide coating [38], the initial sharp change in potential is most likely caused by surface hydration.

It is of interest to compare the change in potential with electron microscopic images of the state of the surface obtained during corrosion.

3.2. Surface analysis of magnesium electrode during the corrosion process

Micrographs of the magnesium surface after different exposure times in a 0.5 mol/L magnesium sulfate solution are shown in Fig. 4. After immersion in the solution, the surface of the magnesium electrode is covered with a dense layer of corrosion products with inclusions of grains (Fig. 4a, 100 μm). As the exposure time increases, the film grows and its structure becomes loose due to cracking. Moreover, in addition to cracking, these films are also characterized by the presence of two layers of different structures, apparently formed sequentially (Fig. 4a, 5 μm).

Comparing these results with the potential change curves, we can see that its maximum negative shift coincides with the maximum cracking of the film. Thus, the photographs

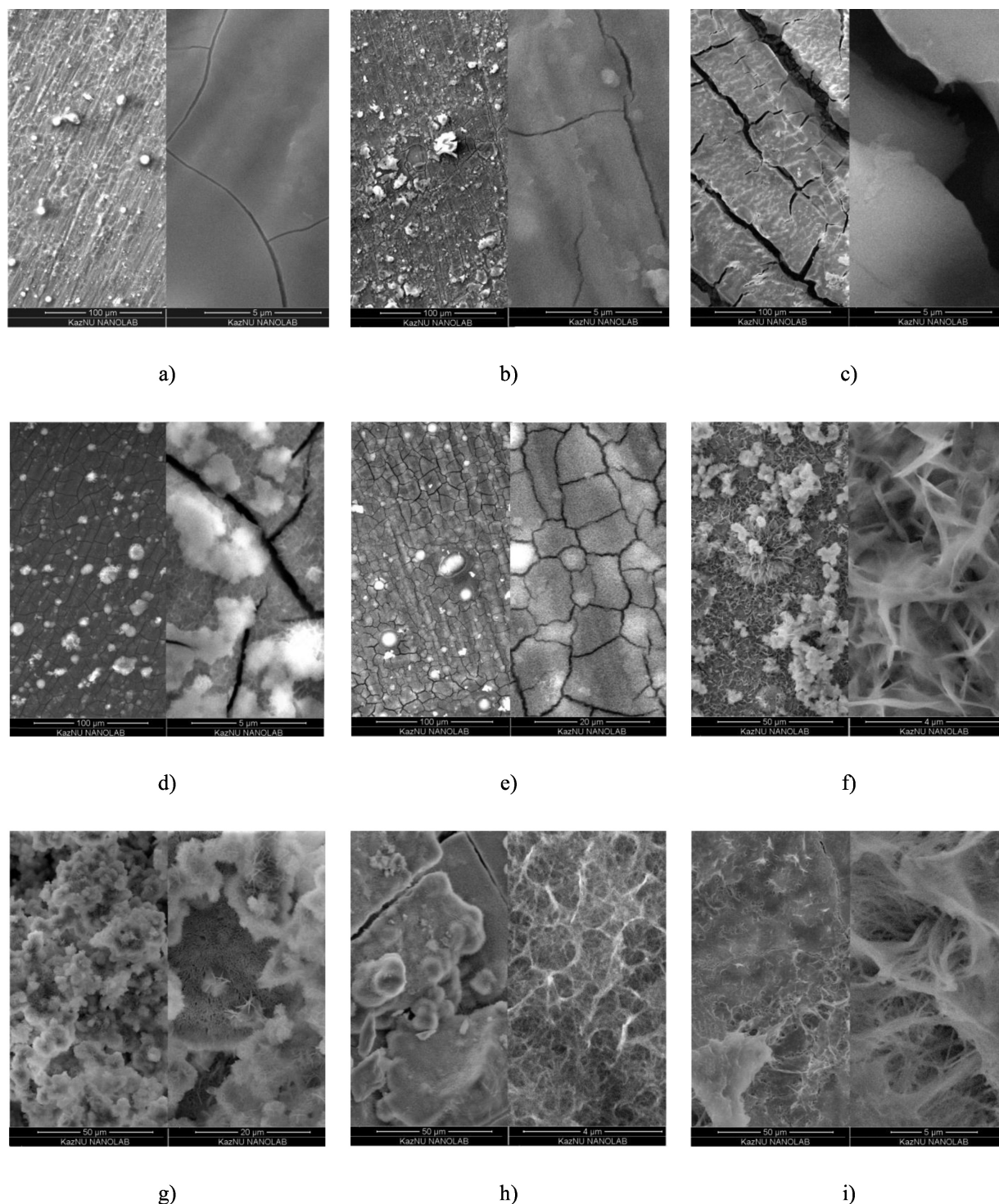


Fig. 4. Micrographs of the surface of the magnesium electrode at different exposure times of the electrode in a solution of 0.5 mol/L MgSO_4 (a) 1 min; (b) 5 min; (c) 10 min; (d) 20 min; (e) 30 min; (f) 12 h; (g) 24 h; (h) 7 days; (i) 1 month.

show that in the region of 10 min of exposure in the solution, there is a pronounced formation of large microcracks in the film (Fig. 4c, 5 μm). In [39,40], this effect is explained by cracking with an increase in the volume of the crystal lattice during the transition of the oxide cubic lattice to the hexagonal $\text{Mg}(\text{OH})_2$. However, the nature of the cracking rather indicates an internal compression of the film with

a seal, which is especially evident at an exposure of 10 min. This rather characterizes the formation of denser magnesium oxide on the surface of magnesium metal [40]. By 30 min of exposure cracks in the film which are formed on the surface with magnesium hydroxide are tightened (Fig. 4e). At a 12 h exposure, noticeable neoplasms grow on the surface in the form of clusters of small needles (Fig. 4f). After 30 days

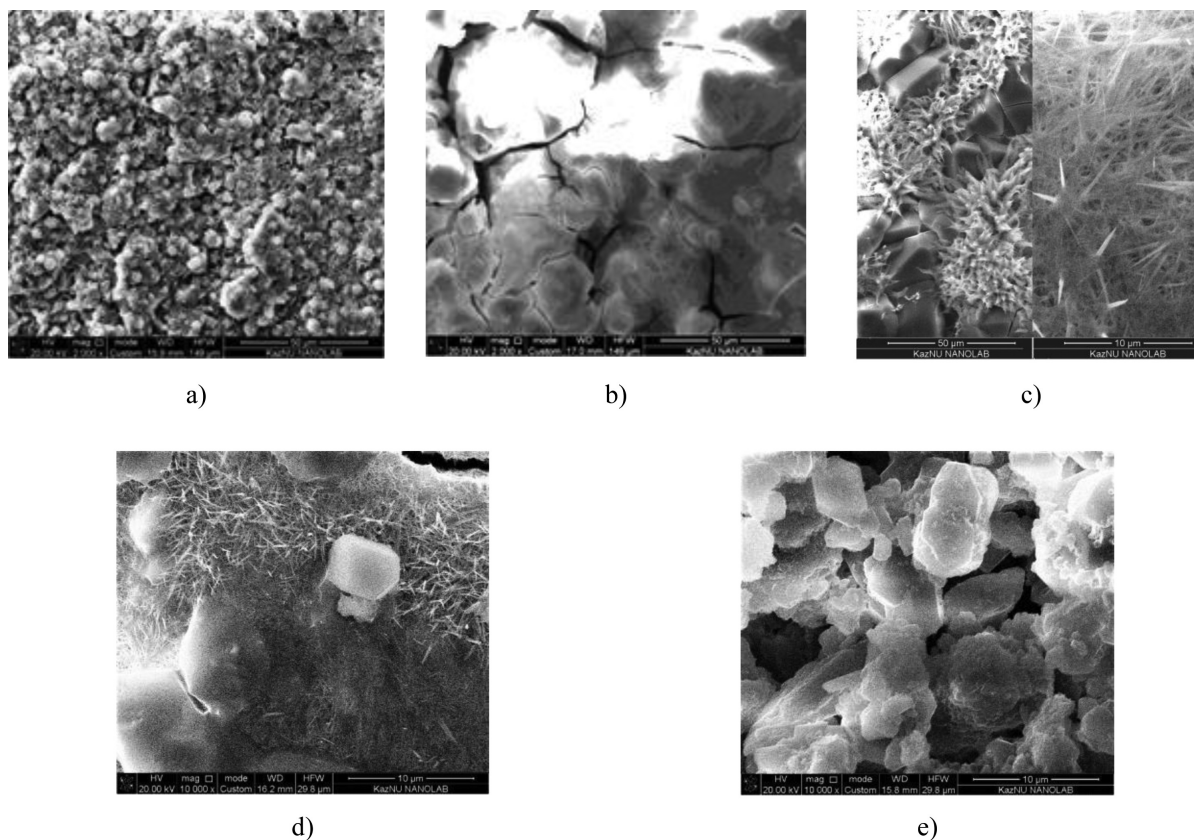


Fig. 5. Micrographs of the magnesium electrode surface at different electrode exposure times in 1 mol/L MgSO_4 solutions: (a) 1 min; (b) 10 min; (c) 30 min; 2 mol/L MgSO_4 : (d) 1 min; (e) 10 min.

of exposure, the film looks like a continuous loose formation (Fig. 4i). The fine structure of the film surface, starting from 30 min of corrosion, is represented by needle-shaped crystals of a nanosized thickness (Fig. 4e, 20 μm), which only increase further, forming regular structures (Fig. 4f, 4 μm). It would be logical to assume that the product of corrosion on the film surface is magnesium hydroxide, which crystallizes from solution by a different mechanism than the bulk of the film as evidenced by its completely different morphology.

With an increase in the concentration of magnesium sulfate in the solution to 1 and 2 mol/L, the corrosion rate of magnesium sharply increases, as seen from the micrographs (Fig. 5). Even after a minute holding in a 1 mol/L solution, a massive loose film is formed on the magnesium surface (Fig. 5a, b). Moreover, the surface of this film has the same fleecy coating as in 0.5 mol/L solutions, which consists of acicular crystals of a nanosized thickness (Fig. 5c). During corrosion for 30 min (Fig. 5c), a coarse-grained coating is formed, which also has needle-shaped formations on the surface. We can even see a greater acceleration of film growth in solutions of 2 mol/L magnesium sulfate (Fig. 5d, e), where the corrosion film becomes continuous and massive already after a minute of metal exposure in solution, and the crystals become larger. In this case, the surface acicular structure turns into a network due to the intergrowth of individual crystals into a continuous array, which corresponds to the formation of denser continuous films during long-term corrosion.

X-ray phase analysis (XRD) of the surface of a magnesium electrode kept in these electrolytes (Fig. 6) showed that in electrolytes containing magnesium sulfate 0.5 mol/L, films containing magnesium oxide and magnesium hydroxide of the brucite structure are formed. In addition, magnesium metal from the substrate is also presented. In 1 mol/L magnesium sulfate, the entire surface is covered with magnesium hydroxide (brucite), which is visible in the spectra against the background of a significant content of the amorphous phase (Fig. 6b), which is also confirmed in micrographs in the form of formations of an acicular modification on an amorphous substrate (Fig. 5c).

The results of X-ray spectral microanalysis (EDAX) of the magnesium electrode surface in magnesium sulfate solutions are shown in Table 1.

After one minute of corrosion of magnesium in a 0.5 mol/L solution the atomic ratio of oxygen to magnesium in the film is even less than 1:1, as it should be for pure magnesium oxide. Then the ratio gradually increases.

Such an analysis result should be considered biased since microanalysis is done to a certain depth. In a thin film this can lead to a magnesium substrate entering the analyzed area and accordingly, to an overestimation of the magnesium content. It must be taken into account when interpreting the data. Following the theory of the method, the penetration depth of the microprobe beam is given by the Kanaya-Okayama formula (6) and is about 3 μm under our conditions.

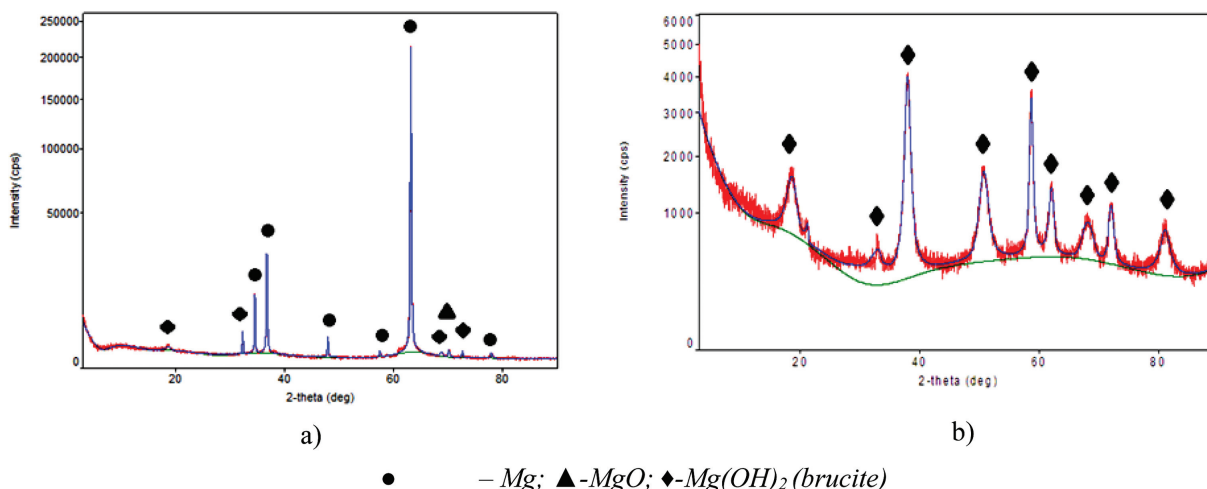


Fig. 6. XRD analysis of magnesium samples kept for 30 min in electrolytes: (a) 0.5 mol/L MgSO_4 ; (b) 1 mol/L MgSO_4 .

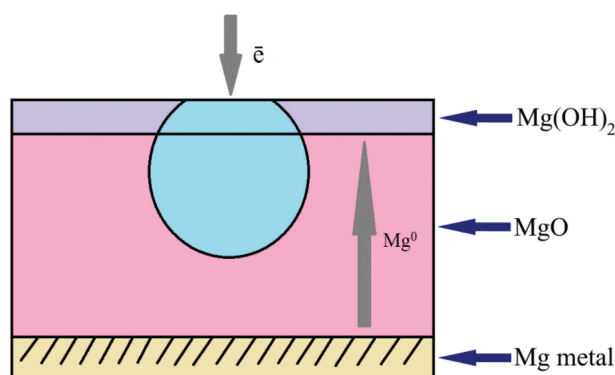


Fig. 7. Geometry of the region under analysis taking into account the structure of the film.

$$R(\mu\text{m}) = 0,0276 \frac{AZ^{-8/9}}{P(\frac{\text{g}}{\text{cm}^3})} E_0^{5/3} (\text{keV}) \quad (6)$$

where R is the maximum range of an electron in the medium, A is the average atomic mass, and Z is the average serial number of the elements of the material, ρ is its density, E_0 is the excitation energy. An explanatory diagram of the geometry of the analyzed area is shown in Fig. 7.

With in the environment of detectable elements, in addition to the expected elements such as magnesium, and oxygen, which characterize magnesium oxide and hydroxide, we also see such elements as sulfur and sodium. An XRD analysis indicates that the film may also contain magnesium sulfate in the form of a crystalline hydrate in addition to magnesium oxide and hydroxide. Taking into account the high concentration of magnesium sulfate in the 1 and 2 mol/L solutions, it can especially be assumed that these are mechanically included in the corrosion precipitate and non-washable residues of magnesium sulfate that precipitated from the electrolyte. In any case, this should contribute to the overall balance of compounds in the film. By examining the XRD data for these cases (Table 2) and considering the results of the microanal-

ysis, it is possible to determine the content of each of these substances.

The meaning of this recalculation was to be able to recalculate the sum of magnesium oxide and hydroxide according to the available atomic content. For example, sulfur, confirmed by XRD analysis in the form of sulfate hexahydrate, we calculated all the components included therein, respectively, in their atomic ratio, after which the remainder was recalculated to the sum of magnesium oxide and magnesium hydroxide.

It should be noted that the amount of magnesium oxide can be overestimated at the initial stages of time since the microprobe penetrates deep enough during the analysis and can capture the metal. The same applies to samples that were kept in sodium sulfate solutions. Sodium was found there, which was present on XRD analysis in the form of sodium sulfite. The calculations were carried out similarly. Table 1 summarizes all these data of the recalculated film composition in the form of already molecular compounds. And Fig. 8 shows the changes in the content of these compounds over time.

The validity of this approach in calculations is confirmed by the element distribution maps (Fig. 9b–d) and electron micrographs (Fig. 9a) presented below.

In the figure, we see the contours of the formed crystals in a solution of sodium sulfate after thirty minutes of exposure. The element maps show that the crystals contain oxygen, sulfur, and sodium. The entire surface is covered with oxide and hydroxide, and the overlaying crystals will contain sodium sulfite, which is displayed on the map by the distribution of sodium and sulfur. Moreover, the distribution of contours of these elements coincides well with the contours in the electron microscopic image (Fig. 9a).

Considering the results of this analysis (Table 1), it was inferred that when the skin structure is exposed to a depth of about 3 microns, the content of magnesium oxide quickly decreases, and the content of hydroxide increases (Fig. 8a). After about 10 min for a solution of 0.5 mol/L magnesium sulfate, a steady state is restored with resistance to the proportion of magnesium oxide. This can be interpreted as a

Table 1
EDAX data and the film composition calculated.

№	Time	Area	Mg %	O %	S %	Na %	X MgO	X Mg(OH) ₂	X MgSO ₄	X Na ₂ SO ₃
0.5 mol/L MgSO ₄										
1	1 min	Film	50.71	48.1	1.19	0	96.82	0.00	3.18	0.00
2	5 min	Film	38.3	61.13	0.57	0	71.88	27.39	0.74	0.00
3	10 min	Film	34.55	62.84	2.6	0	61.47	34.19	4.34	0.00
4	20 min	Film	37.61	61.36	1.03	0	70.19	28.40	1.42	0.00
5	30 min	Film	37.74	61.38	0.89	0	70.59	28.21	1.20	0.00
6	60 min	Film	38.4	60.84	0.77	0	71.77	27.19	1.04	0.00
0.5 mol/L Na ₂ SO ₄										
7	1 min	Film	97.18	2.82	0	0	100.00	0.00	0.00	0.00
8	5 min	Film	89.08	10.92	0	0	100.00	0.00	0.00	0.00
9	10 min	Film	91.8	8.2	0	0	100.00	0.00	0.00	0.00
10	20 min	Film	82.73	17.27	0	0	100.00	0.00	0.00	0.00
11	30 min	Film	71.01	23.2	1.27	4.52	91.41	0.00	0.00	8.58
12	60 min	Film	61.48	33.9	1.24	3.38	94.93	0.00	0.00	5.07
1 mol/L MgSO ₄										
13	1 min	Film	34.1	63.54	1.92	0	63.40	33.86	2.75	0.00
14	10 min	Film	33.11	64.72	1.82	0	62.45	35.11	2.44	0.00
15	30 min	Film	29.63	66.75	3.26	0	52.74	42.22	5.03	0.00
2 mol/L MgSO ₄										
16	1 min	Film	29.13	66.15	4.42	0	43.79	47.40	8.82	0.00
17	10 min	Film	18.75	73.8	6.92	0	10.04	74.85	15.11	0.00
18	30 min	Film	23.81	70.83	5.08	0	35.21	55.86	8.93	0.00
1:1										
№	Time	Area	Mg, %	O, %	S, %	Na, %	X MgO	X Mg(OH) ₂	X MgSO ₄ *6H ₂ O	X Na ₂ SO ₄
19	1 min	Film	90.73	6.85	0	0	0.00	0.00	0.00	0.00
20	1 min	Formation	38.2	51.19	1.84	3.46	83.22	0.00	0.34	5.37
21	5 min	Film	12.19	48.99	13.39	21.18	0.00	0.00	20.91	79.09
22	5 min	Formation	31.78	57.99	5.89	1.29	0.00	0.00	63.23	7.78
23	10 min	Film	21.98	58.34	0.16	2.33	25.91	1.42	0.00	4.92
24	10 min	Formation	73.81	24.1	0.53	1.56	96.57	0.00	0.00	3.43
25	20 min	Film	36.53	56.83	4.14	0.37	0.00	0.00	64.89	3.04
26	20 min	Formation	52.94	39.54	1.06	0.41	55.47	0.00	5.51	1.32
27	30 min	Film	34.08	51.45	9.07	2.82	0.00	0.00	74.73	13.76
28	30 min	Formation	60.39	32.72	0.71	1.49	77.19	0.00	0.00	3.63
29	60 min	Film	22.15	63.62	9.26	2.73	0.00	0.00	77.90	13.47
30	60 min	Formation	36.12	52.45	1.43	3.51	80.77	0.00	0.00	5.20

rapid increase in the hydroxide part of the skin at the beginning with a constant change in the parameters of the analysis zone. We can see from the micrographs that the transition to the steady state after exposure for 10 min is assumed with the possibility of film cracking. At the same time, an increase in the content of magnesium sulfate in solution leads to a strong increase in the growth rate of the hydroxide part of the skin in the first minute and its more rapid growth in the future.

The formation of oxide can occur at the inner boundary of the film with metallic magnesium according to the Cabrera – Mott mechanism, the implementation of which during the corrosion of magnesium in aqueous solutions was concluded in [8]. An increase in the proportion of the hydroxide and a decrease in the oxide part of the film in the initial period

indicate the hydration of the oxide and its transition to the hydroxide.

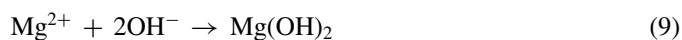
A small amount of magnesium oxide is formed in the air (primary film) on the clean magnesium surface [8,9]. When a magnesium atom from a metal diffuses through a film of magnesium oxide during corrosion, reacting with water molecules on the surface, magnesium hydroxide is formed. Magnesium hydroxide is also formed due to the hydration of MgO [38].

The evolution of hydrogen during corrosion is accompanied by the formation of OH⁻ ions, which also leads to the formation of Mg(OH)₂ on the magnesium surface according to the reaction [41]:

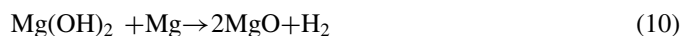


Table 2
XRD data of magnesium surface in different electrolytes.

№	Electrolyte	Time	Phase	Crystal lattice parameters				
					a(Å)	b(Å)	c(Å)	V(Å ³)
1	0.5 mol/L MgSO ₄	30 min	Mg(OH) ₂ (brucite)	Standard	3.14	3.14	4.76	40.95
				Experiment	3.14	3.14	4.73	40.45
		24 h	Mg(OH) ₂ (brucite)	Standard	3.14	3.14	4.76	40.9
				Experiment	3.14	3.14	4.73	40.45
		9 days	Mg(OH) ₂ (brucite)	Standard	3.14	3.14	4.76	40.9
				Experiment	3.15	3.15	4.79	41.09
2	1 mol/L MgSO ₄	1 min	MgSO ₄ ·6H ₂ O	Standard	9.97	7.19	24.27	1719.08
				Experiment	10.11	7.21	24.41	1761.44
		30 min	MgSO ₄ ·6H ₂ O	Standard	9.97	7.19	24.27	1719.08
				Experiment	10.11	7.21	24.41	1761.44
		9 days	Mg(OH) ₂ (brucite)	Standard	3.14	3.14	4.76	40.9
				Experiment	3.15	3.15	4.79	41.09
3	0.5 mol/L Na ₂ SO ₄	30 min	Na ₂ SO ₃	Standard	5.45	5.45	6.16	162.63
				Experiment	5.54	5.54	6.16	163.67
			MgO	Standard	3.27	3.27	4.87	45.37
				Experiment	3.79	3.79	3.79	54.49
		9 days	Mg(OH) ₂ (brucite)	Standard	3.14	3.14	4.76	40.9
				Experiment	3.15	3.15	4.79	41.09
4	1:1	30 min	Na ₂ SO ₃	Standard	5.45	5.45	6.16	162.63
				Experiment	5.54	5.54	6.19	164.83
			MgO	Standard	3.27	3.27	4.87	45.37
				Experiment	3.57	3.57	4.23	46.91
		9 days	Mg(OH) ₂ (brucite)	Standard	3.14	3.14	4.76	40.9
				Experiment	3.15	3.15	4.79	41.09



All these transformations increase the hydroxide content of the film surface, which is especially pronounced at later stages, especially at high electrolyte concentrations. At the same time, when magnesium is corroded in 0.5 mol/L magnesium sulfate up to 1 h after the initial sharp drop, a weak stable increase in the magnesium oxide content in the surface layer with a depth of about 3 microns is recorded, which can only be explained by a decrease in the thickness of the magnesium hydroxide layer on the surface. The reason for this behavior may be the transformation of magnesium hydroxide into oxide at the oxide-hydroxide interface during its interaction with metallic magnesium diffusing through the film following the reaction [17,29].



The transfer of a magnesium atom through the film is ion-electronic, and then the interaction with magnesium hydroxide will go through the stage of its interaction with an electron diffusing through the oxide layer under the action of a chemical potential gradient. In addition, considering the deep cracking of the film by this time, the appearance of anodic regions, which have been researched in numerous studies [17,29,42,43], cannot be ruled out. This suggests a reduction of the hydroxide by an electron transferred through the film in a cathodic process with the same result.

Magnesium oxide at the outer boundary of the film undergoes hydration with the formation of magnesium hydroxide, and the difference in the rates of the processes of oxide formation and its hydration with the formation of hydroxide determines the ratio of the sizes of these phases in the analyzed layer. The patterns of this transformation determine the patterns of magnesium corrosion in aqueous electrolytes since in this case a new phase with its morphological characteristics is formed, and the further process will also be determined by the transfer of water molecules through this layer to continue the hydration process. Works on the study of magnesium oxide hydration are presented quite widely [44,45]. For example, Smithson et al. [44] in studying the hydration kinetics of magnesium oxide suggested that the process is determined by the kinetics of transformation at the interface and is described by the model of a contracting core on individual MgO particles. The authors of [16] also came to a similar conclusion, corrected for the effect of material porosity. At the same time, the occurrence of a diffusion limitation for water transport is indicated when a layer of magnesium hydroxide of considerable thickness grows. When studying the hydration process in the presence of various electrolyte salts, it was found that in the presence of magnesium sulfate, the hydration rate is significantly accelerated, which correlates with an increase in the solubility of magnesium hydroxide in a solution of magnesium sulfate up to 5.2 g/L, in contrast to its solubility in water 0.012 g/L [46]. In this regard, a sharp increase in the corrosion rate with an increase in the concentration of magnesium sulfate becomes understandable. The reason is an increase in the rate of hydration of magnesium oxide due to the disso-

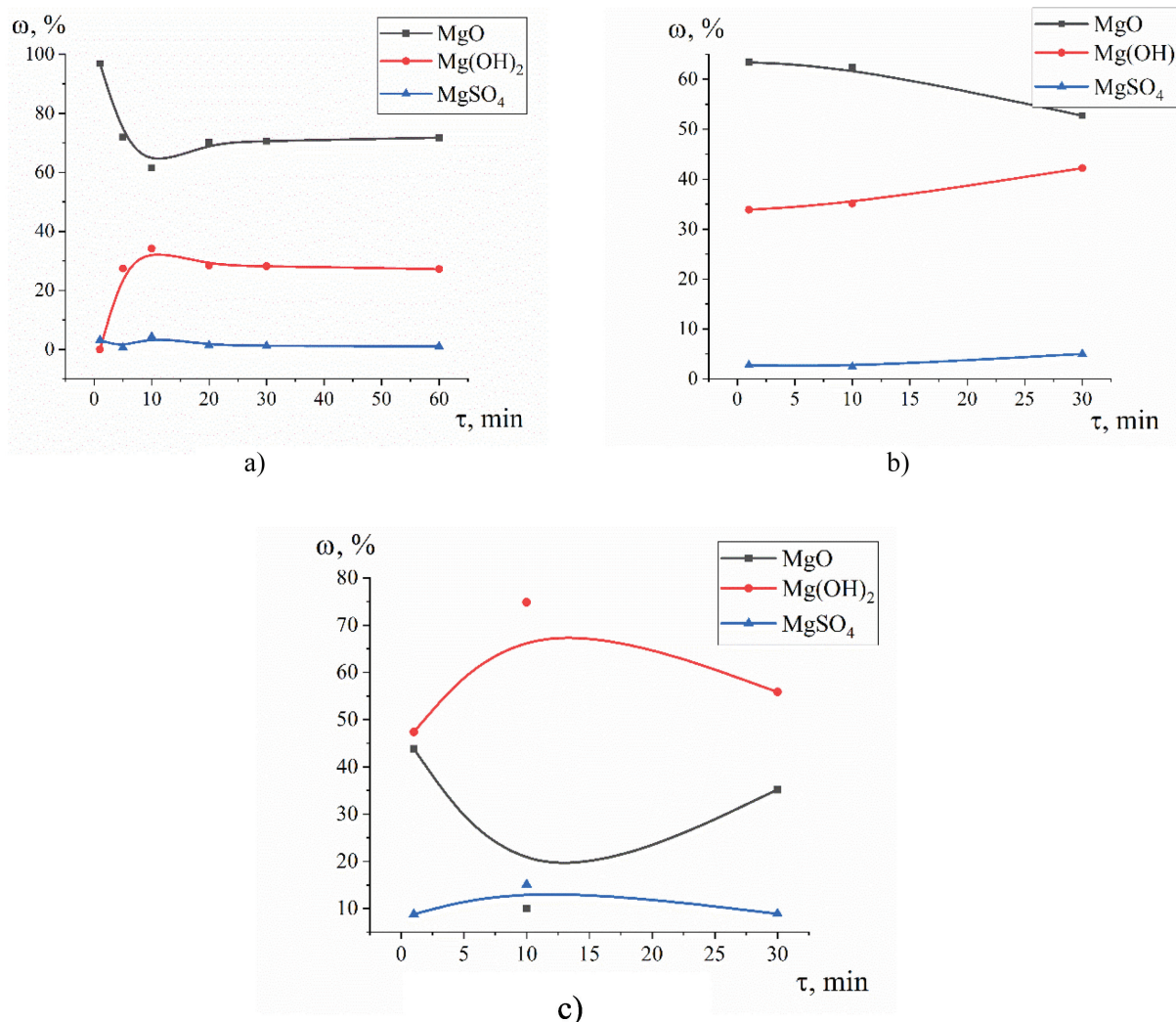


Fig. 8. Time changes in the content of basic compounds in the corrosion film of magnesium in: (a) 0.5 mol/L MgSO₄; (b) 1 mol/L MgSO₄; (c) 2 mol/L MgSO₄.

lution of the resulting hydroxide. These studies also indicate the formation of acicular crystals of magnesium hydroxide (brucite) on the surface of magnesium oxide as a result of its crystallization.

This is what is seen in electronic images of the surface of corroding magnesium in later stages.

It is known that in solutions of magnesium sulfate during hydration, sulfate is introduced into magnesium hydroxide with the formation of a solid solution. For example, in a 5% solution of MgSO₄, a solid solution of the composition $[\text{Mg}(\text{OH})_{1.86} \cdot (\text{SO}_4)_{0.07}] \cdot 0.23\text{H}_2\text{O}$ [47] is formed. It is also noted that amorphization of hydration products also occurs, including the formation of continuous arrays, which is seen on the micrographs of the surface in 1 and 2 mol/L solutions of magnesium sulfate (Fig. 5) along with the formation of solid solutions,

The highly soluble solid solutions and amorphous phases formed after hydration subsequently crystallize in the form of hydroxide of the brucite morphology, which is reflected both as needles on electron microscopic images (Fig. 5c), and in

XRD from the content of the amorphous phase (Fig. 5e). In addition, the results of the analysis indicate the content of a significant amount of magnesium sulfate, especially at long exposure times and its high concentration in solution, while its separate phase is not detected. At the same time, the deviation of the parameters of the crystal lattice of brucite from the passport value confirms the inclusion of sulfate in the hydroxide structure (Table 1).

In a sodium sulfate solution, magnesium corrosion proceeds somewhat differently (Fig. 10). In this electrolyte, there is no obvious cracking of the film and no intense evolution of hydrogen during anodic polarization, as in a solution of magnesium sulfate. With an increase in the exposure time of the metal in the electrolyte, relatively uniform growth of the film occurs over the entire surface of the metal. EDAX of the film in sodium sulfate solution showed that it contains Mg, Na, S, and O (Table 1). Moreover, XRD showed that there is a separate Na₂SO₃ phase (Fig. 11). The calculation of the film composition based on the results of EDAX, taking this into account, shows that the magnesium content is

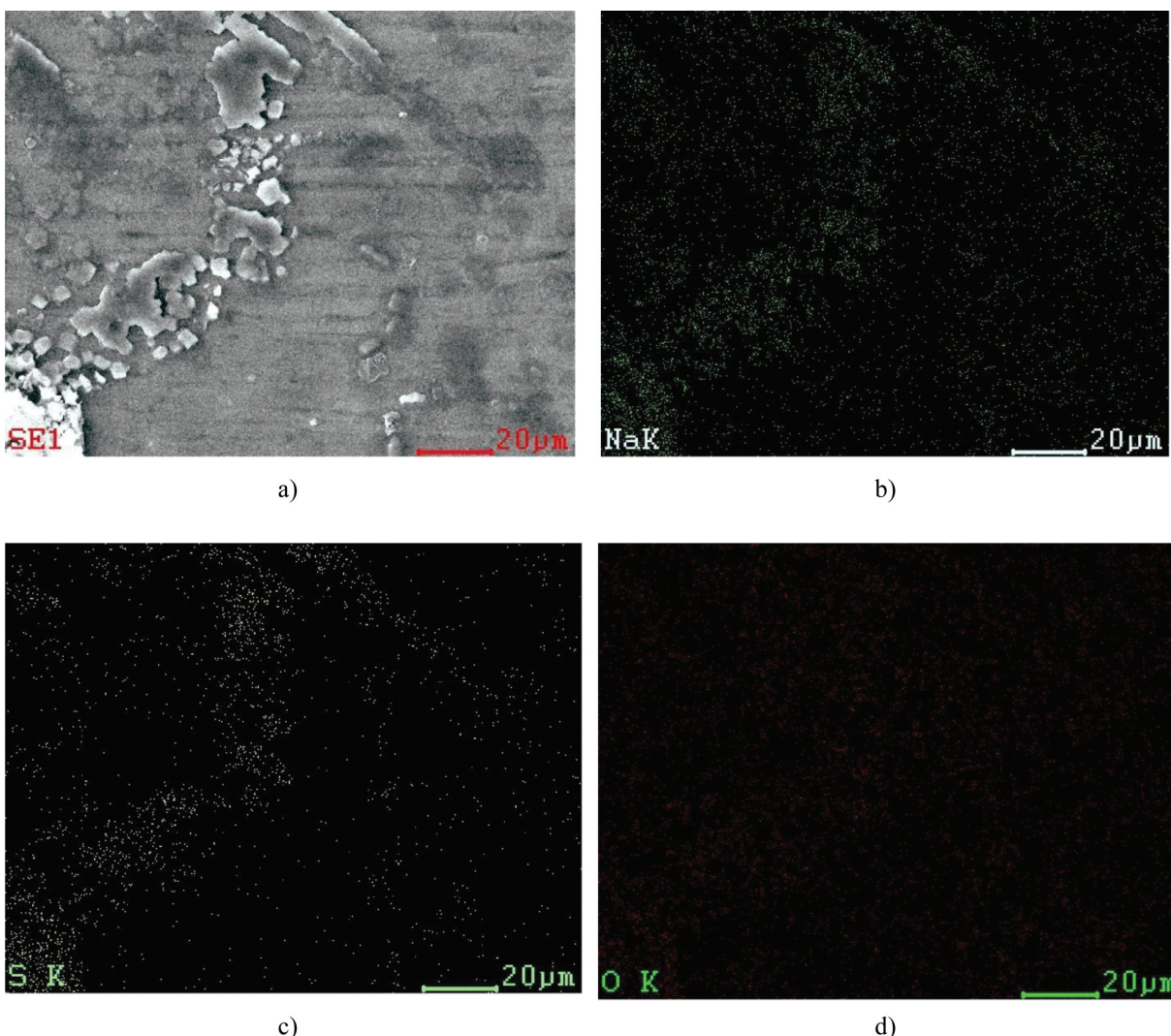


Fig. 9. Map of the distribution of elements on the magnesium surface after soaking in 0.5 mol/L Na_2SO_4 electrolyte (a) analyzed surface; (b) sodium distribution; (c) sulfur distribution; (d) oxygen distribution.

overestimated for the first half an hour, which indicates a very small film thickness when the substrate material is also captured in the analysis. We see the evidence of this in the photographs.

The presence of Na and S in the film is most likely due to the formation of solid solutions of sodium sulfate in magnesium hydroxide, similar to that indicated above for a solution of magnesium sulfate, which is confirmed by a change in the lattice parameters of brucite.

Of particular interest is the formation of sodium sulfite, since the sulfate ion is quite resistant to reduction in solutions and the evolution of hydrogen begins before the reduction of the sulfate anion. Most likely, such a transformation is possible only in the solid phase during reduction. This reduction is carried out by a magnesium atom or an electron diffusing through the film, as shown above.

Corrosion of magnesium in an electrolyte containing 0.5 mol/L MgSO_4 and 0.5 mol/L Na_2SO_4 is more similar to the corrosion in magnesium sulfate, as seen in Fig. 4, but is more accelerated.

Initially, the metal undergoes significant corrosion, which can be seen in Fig. 12 by the cracks and growths formed on the metal surface already in the first minutes of corrosion (Fig. 12a).

The fine structure of the surface of corrosion films in a mixed electrolyte is of particular interest which is a very porous form of a sheet array-oriented normally to the surface. In this case, the macro relief becomes inhomogeneous and is characterized by swelling, leveling off after a week of corrosion.

To compare the compositions of different parts of corrosion films on the magnesium surface during corrosion in different electrolytes, X-ray spectral microanalysis was carried out at individual points of the film surface, the results of which are presented in Table 1. The analyzes were carried out: 1 on a flat film surface, 2 in film growths (bumps). According to the EDAX data (Table 1), it can be concluded that the film composition is primarily affected by the morphology of the corrosion film sections. Thus, zones of continuous uniform coatings in solutions containing sodium have

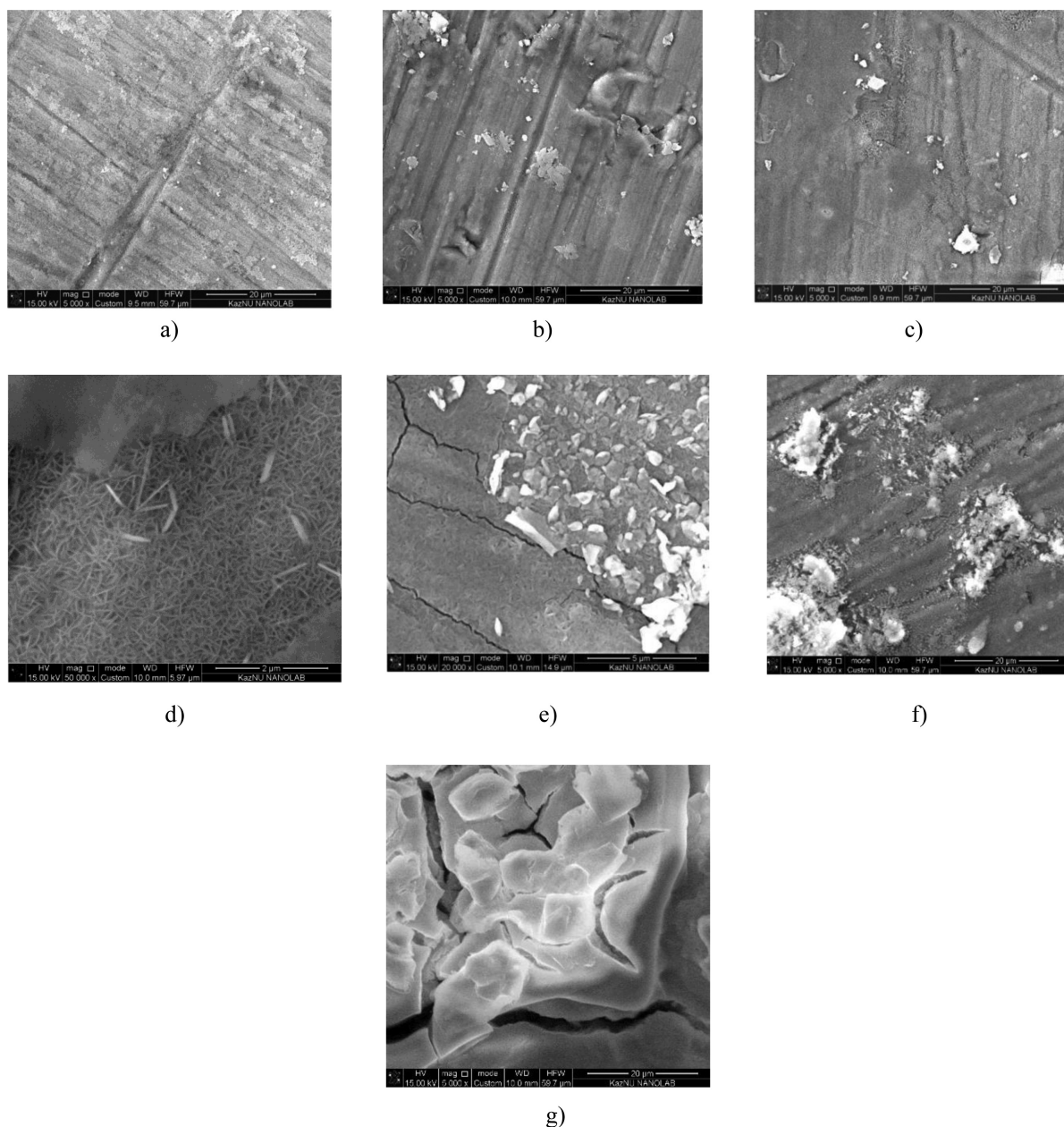


Fig. 10. Micrographs of the surface of the magnesium electrode at different exposure times of the electrode in a solution of 0.5 mol/L Na_2SO_4 (a) 1 min; (b) 5 min; (c) 10 min; (d) 20 min; (e) 30 min; (f) 12 h; g) 24 h.

a composition of the surface layer close to magnesium oxide, in contrast to a solution of magnesium sulfate, where the composition is almost hydroxide. The reason for this behavior may be the high solubility of magnesium hydroxide in electrolytes containing sodium salts, as indicated in [37]. The presence of magnesium salts in the solution leads to the cracking of the continuous film, and the film is very thin at the site of the crack, resulting in an overestimated magnesium content. The formed friable growths, characteristic of the mixed electrolyte and resembling pitting, also consist mainly of magnesium hydroxide in the surface analyzed layer.

The presence of sufficiently thick films on a corroding metal makes it possible to carry out gravimetric study of the

process. The mass of the corrosion film was determined by calculating the mass gain of the washed and dried magnesium sample. The negative value of the mass gain is associated with both the process of shedding of the loose part of the film mass and its dissolution during recrystallization with subsequent diffusion into the depth of the solution. Even the presence of a protective bag holding on top does not completely stop the diffusion and the exit of a part of the dissolving film beyond the limits (see the explanation in the text). The calculation of the metal mass loss during corrosion was determined by the mass loss when the corrosion film was completely removed from the sample surface without destroying the metal base itself. Fig. 14 shows the dependence of the amount of corroded metal on time. This dependence graph was differ-

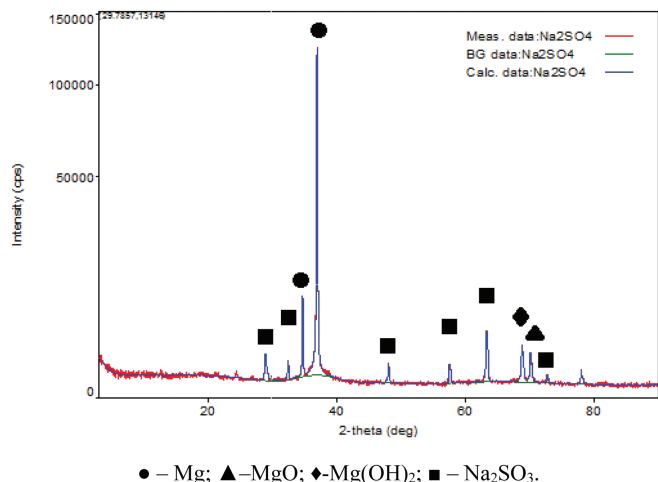


Fig. 11. XRD analysis of magnesium samples kept in electrolyte 0.5 mol/L Na_2SO_4 .

entiated to find the corrosion rate. The amount of metal was converted into the amount of electricity corresponding to this metal under the condition of the formation of divalent magnesium. These dependences in the form of corrosion current mA/cm^2 are shown in Fig. 16. In order to more clearly show the initial areas where a small amount of dissolving metal is represented and the definition is given with a large error, the corrosion current was determined by the dependence of the hydrogen released on time.

The results of the gravimetric analysis of corrosion, shown in Fig. 13, indicate that after a month of corrosion, a decrease in the mass of the corrosion film is observed in all the electrolytes under study, while in the first few days its growth was observed first, which was the smallest in sodium sulfate and the largest in 2 mol/L magnesium sulfate solution, which correlates with SEM data on film growth in the first hours of corrosion.

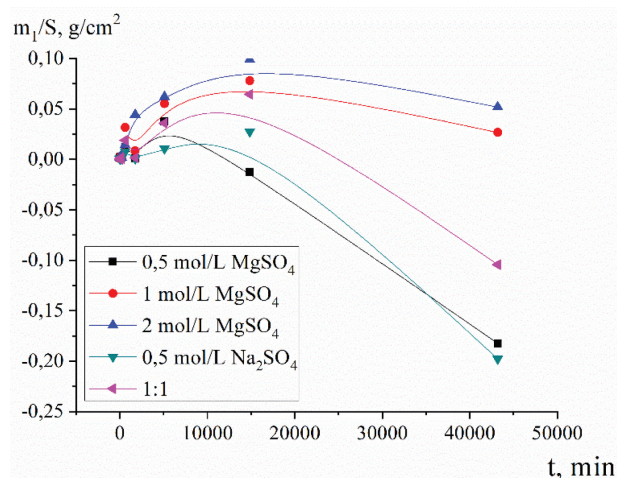
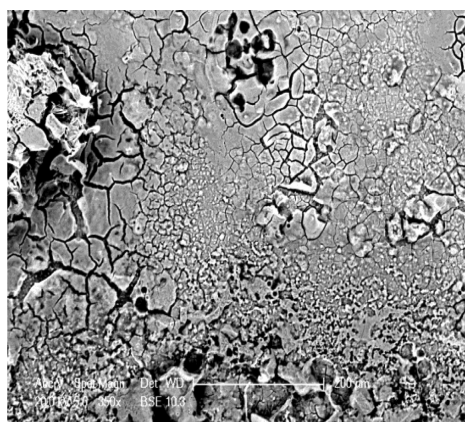


Fig. 13. Change in the mass of corrosion films on magnesium in different electrolytes during corrosion.

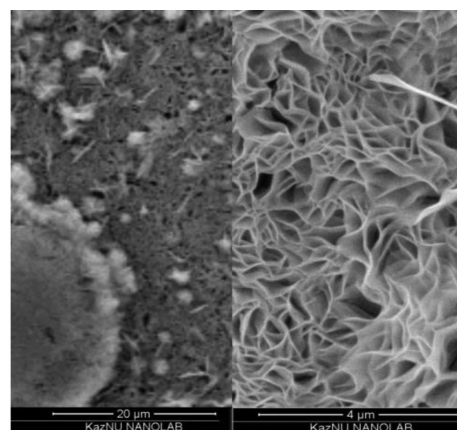
As a result of an increase in the thickness of the corrosion layer, it is quite natural to slow down the rate of formation of a corrosion product due to the occurrence of diffusion restrictions in the transfer processes, however, this ultimately implies an equalization of the rates of formation and dissolution of corrosion products, i.e. inhibition of film growth. But this does not explain the decrease in the mass of the corrosion film, especially to negative values.

Such an alternating course of change in the mass of the film indicates a change in the balance between two processes the formation of a corrosion product and its dissolution due to the different dependence of the rate of these processes on time.

The decrease in the mass of the corrosion film during corrosion can be explained by shedding from the surface of a corrosion product that is poorly associated with it, which was observed for all electrolytes at the later stages of corrosion development. The time of appearance of this precipitate in



a)



b)

Fig. 12. Micrographs of the surface of a magnesium electrode at different exposure times of the electrode in a solution of 0.5 mol/L MgSO_4 + 0.5 mol/L Na_2SO_4 (a) 5 min; (b) 24 h.

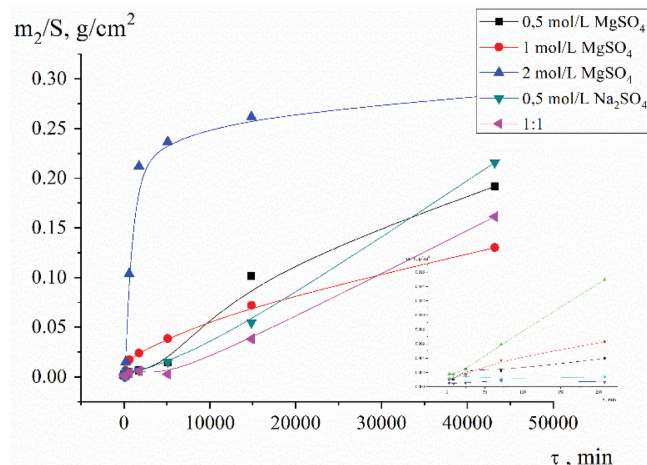


Fig. 14. Total mass loss of metallic magnesium during corrosion in different electrolytes.

the vessel approximately corresponds to the position of the maximum on the curves of the dependence of the mass of the corrosion film on time.

XRD analysis of all samples of the precipitate that fell off the electrode showed that it was crystalline magnesium hydroxide-brucite. To collect the crumbling precipitate, magnesium samples were placed in bags made of a thin mesh of an inert polymer, followed by a determination of the mass and composition of the product. At the same time, it was noted that the formation of a precipitate occurs not so much due to shedding from the surface of magnesium, but by the mechanism of precipitation from the solution, since the precipitate was also formed outside the bag, depositing on the bottom of the beaker with electrolyte, in which the bag with the magnesium sample was hung.

The XRD of the corrosion film presented in Fig. 6 and their micrographs in Fig. 5 indicate the presence of crystalline magnesium oxide and brucite, as well as a significant amount

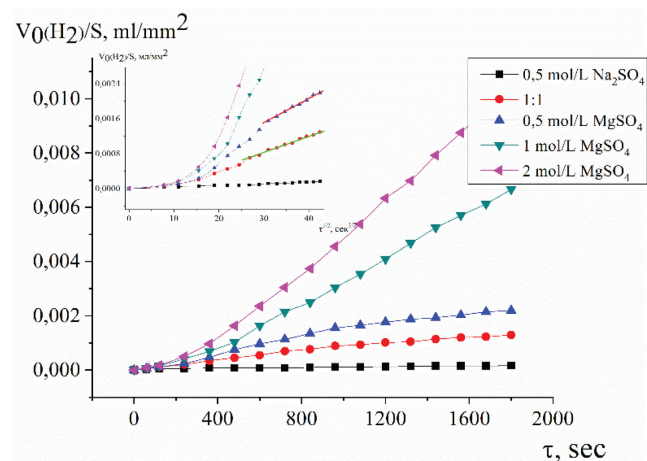


Fig. 15. Dependence of the volume of evolutiond hydrogen on time in different electrolytes.

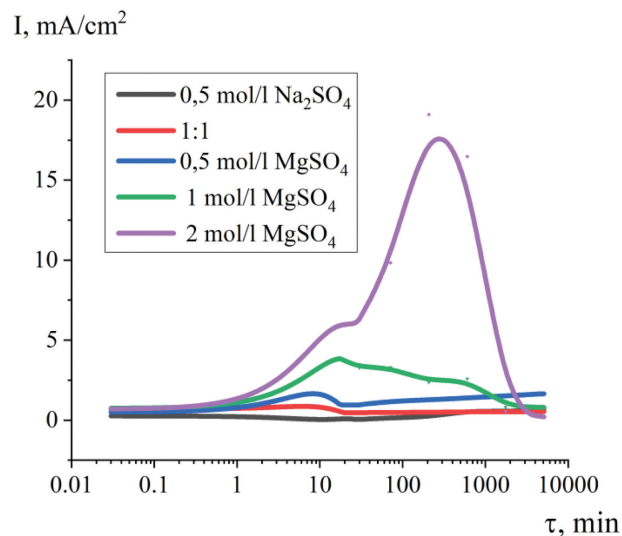


Fig. 16. Dependence of the corrosion rate of magnesium in different electrolytes on time.

of the amorphous phase. Most likely, magnesium hydroxide, which is formed upon oxide hydration, is amorphous [45].

A strong amorphization of the products of hydrolysis of magnesium oxide in sulfate electrolytes and a strong increase in the solubility of magnesium hydroxide in solutions of magnesium sulfate and other salts are indicated in [47].

In kinetic studies of the hydrolysis of magnesium oxide [46], it was concluded that the kinetics is limited by the slowness of the dissolution of hydroxide from the surface of magnesium oxide. In salt solutions with higher hydroxide solubility, this process is accelerated.

Taking into account the formation of a brucite phase with an acicular structure on the surface of corroding magnesium in all studied solutions, as well as indications of the same in [48], it can be assumed that the crystallization of brucite occurs from the supersaturation zone in the solution. Over-saturation of the solution with the crystalline phase of brucite is created due to the dissolution of amorphous magnesium hydroxide, which has a high solubility.

For the gravimetric determination of the corrosion rate, the mass loss of metal samples was also determined during the thorough mechanical removal of all corrosion deposits from the surface (Fig. 14).

Initially, the change in mass due to corrosion is minimal, and, accordingly, the error in determining the mass is quite large, especially when it comes to the mass of metal consumed, we used a different approach to determine the mass at the beginning of the process from the evolutiond hydrogen. The evolutiond hydrogen was collected in a standard way in a burette, as described in the methodological part, in the initial period of up to thirty minutes. Fig. 15 shows the dependence of the volume of evolutiond hydrogen on time, and the inset shows the dependence of this volume on the square root of time, that is, in the coordinates that determine the parabolic course of corrosion film growth.

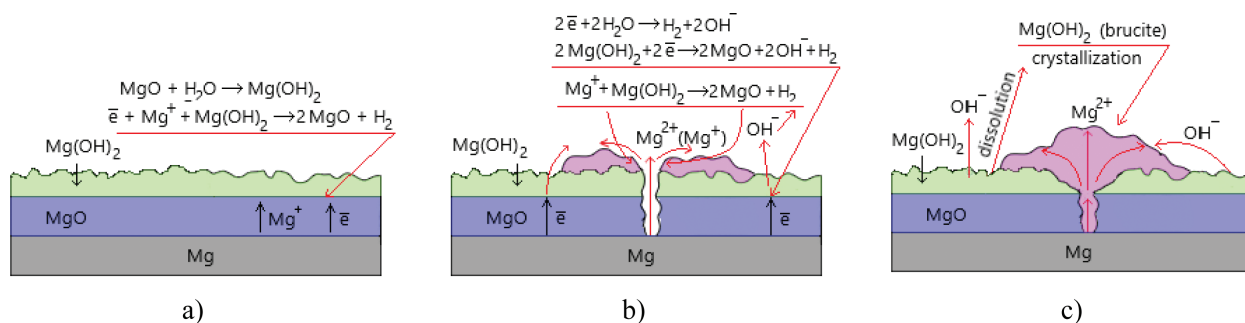


Fig. 17. Scheme of magnesium corrosion in aqueous electrolytes.

The regularities of the rate of hydrogen evolution depict the regularities of the growth of the mass of the film under the condition of the insolubility of the product and the rate of corrosion of the metal. At high concentrations of magnesium sulfate in the electrolyte, 1 and 2 mol/L, the dependence of the volume of hydrogen on time is practically linear. At lower concentrations in the mixed electrolyte and magnesium sulfate, clear linear sections are observed in the dependence of the hydrogen volume on the square root of time, describing the parabolic growth of the film. We also pointed out a similar dependence in the study of the polarization characteristics in these solutions [37]. From the obtained dependences of the volume of hydrogen on time, curves of the dependence of the corrosion current on time were obtained by transformation, and these parts in the initial sections were compiled with the general dependences for the corrosion currents calculated from the mass loss of the magnesium electrode over time, as shown in Fig. 16. From Fig. 16 the corrosion rate varies greatly for different concentrations of magnesium sulfate. Nevertheless, after a sufficiently long time of more than 3000 min, the corrosion rate is practically leveled, and all curves converge at approximately the same level, demonstrating approximately the same corrosion rate, regardless of the concentration and type of electrolyte.

Fig. 16 shows the dependence of the corrosion rate of magnesium in different electrolytes. The highest corrosion rate is observed in a solution of 2 mol/L magnesium sulfate, and as its concentration decreases, it naturally decreases, especially in the initial stages of corrosion (inset, Fig. 15). In all electrolytes based on magnesium sulfate, the dependence of the corrosion rate on time is characterized by a maximum. In this case, the higher the electrolyte concentration, the later the maximum corrosion rate is reached. In a solution of sodium sulfate and a mixed electrolyte, the corrosion rate decreases monotonically, and after a month, the corrosion rates in all electrolytes become close.

A similar final state of the surface in different electrolytes is most likely associated with the formation of a continuous layer of brucite on the electrode surface, and the presence of a maximum is determined by the transition from the tendency of loosening and shedding of the film to the formation of a dense layer of brucite.

4. Conclusions

The processes occurring in the magnesium-film-water system during corrosion are ultimately influenced by the complex mechanism of film formation and hydrolysis of magnesium oxide. One of the key points here is the problem of particle transport in the solid phase, which provides a corrosion process. Formally, these are magnesium atoms diffusing from the metal through the film to the interface with the electrolyte. The idea proposed in [40,49] on the formation of magnesium oxide at the interface between magnesium and magnesium oxide involves the movement of an oxygen ion through an oxide film. The transfer of magnesium cation through the film in the opposite direction seems more realistic. This most likely cation is the Mg^+ cation, which is the result of the dissociation of the magnesium atom in its oxide phase and exists only in this medium, reacting with both water and magnesium hydroxide on the surface of the oxide phase. Moreover, such a cation is most likely the Mg^+ cation, which, is the result of the dissociation of the magnesium atom in the phase of its oxide and exists only in this environment, reacting with both water and magnesium hydroxide on the surface of the oxide phase.

Fig. 17 shows the development of this process within this paradigm. As has already been shown in the analysis of the formation of the initial phases of corrosion films, the process has regularities described by the Mott law [8]. In this case, the primary film formed during the preparation of the electrode, from which corrosion begins after immersion in an aqueous solution, determines the beginning of this process. Under these conditions, a relatively even and dense layer of the primary film is additionally formed on the surface. The first stage corresponds to the formation of this particular part of the film and corresponds to the initial negative shift of the potential. At the same time, a new hydroxide layer is formed on the surface of the oxide film due to the hydrolysis of the oxide and the reduction of water. Thus, by the end of the initial film formation, there is already a two-layer film with a hydroxide surface coating. And already here, from the early stages, the formation of a balance begins between the formation of an oxide film during the interaction of the monovalent magnesium cation and an electron with the surface hydroxide and its hydrolysis. From these early stages, the formation of a balance between the formation of an oxide film dur-

ing the interaction of a monovalent magnesium cation and an electron with a surface hydroxide and its hydrolysis also begins. In Fig. 17a of this diagram, this process is shown when a monovalent magnesium cation diffusing through the oxide layer of the film reacts with the hydroxide film, reducing it with hydrogen evolution and oxide formation. A similar process occurs with an electron diffusing through the oxide film, which also interacts with hydroxide and water. This process of converting magnesium hydroxide to oxide is balanced by the process of hydration of the oxide with water and reduction of water, which occur due to the diffusion of water through the outer layer of hydroxide, since the latter is not very dense, as can be seen from electron microscopic images. And, in principle, the onset of quasi-equilibrium is possible here, when the hydration rates would equalize with the rate of conversion of hydroxide into oxide. The most important difference, similar to corrosion that occurs after cracking, is the formation of separated sections of the anode and cathode, where the role of the anode is played by the cracks and depressions formed, and the cathode process is distributed over a flat surface of the hydroxide film. Migration also contributes more to mass transfer, as shown in Fig. 17b. At the same time, not only diffusion mass transfer, but also migration mass transfer from anode to cathode, from cathode to anode begins to play a significant role in the formation of relief. As a result, these two streams form magnesium hydroxide, the formation of which occurs at a distance from the cathode and anode sections. This distance depends on the mobility of the corresponding ions in the solution (Fig. 17c).

This leads to the formation of a complex balance in the corrosion film, which is also superimposed by the recrystallization of amorphous and finely dispersed magnesium hydroxide into crystalline brucite.

The mechanism of the recrystallization process consists of the dissolution of amorphous or finely dispersed hydroxide, highly soluble in the presence of magnesium and sodium salts, and its subsequent crystallization in the form of brucite or a solid solution of salts in it from the electrolyte, as shown above. This process is of great importance, as a loose crumbling layer is formed, which does not slow down corrosion [36].

The characteristics of charge transfer through the film, as we have shown earlier [36], are mainly determined by the dense part, which includes only the part adjacent to the metal, consisting of magnesium oxide and the dense part of the hydroxide layer on its surface. The overlying layers of crystalline brucite have a loose morphology and little determines the polarization. This is the main reason for the strong change in the electrical characteristics in the initial period when the formation of a two-layer dense part of the film occurs. In general, the corrosion rate of pure magnesium in these solutions is high, and the mechanism of the process does not provide sufficient passivation of the metal by corrosion products. It is demonstrated by the dependence of the corrosion current on time passing through a maximum and reaching a stationary value, little dependent on the composition of the solution. This is a direct confirmation of the fact that the process begins

to be determined by the balance between the dense oxide and hydroxide parts with an insignificant influence of the surface part of the openwork brucite sediment.

Acknowledgments

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