The influence of technological factors on electrochemical characteristics of cast magnesium cathodic protective elements

V. Kechin,^{1*} E. Lyublinski^{2**} and A. Kireev¹

¹Vladimir State University, ul. Gor'kogo, 87, Vladimir, 600000 Russian Federation ²COR/SCI, LLC, 6421 Dorset Ln., Solon, OH 44139, USA *E-mail: <u>kechin@vlsu.ru</u> **E-mail: elyublinski@gmail.com

Abstract

Cathodic protection systems with magnesium cast sacrificial anodes are widely used for corrosion protection of metallic structures in sea water and soil. The accumulated experience in the application testifies to the dispersion of current capacity (CC) values up to 20%. As a result, the service life and economic efficiency of protection is unpredictable. Magnesium alloys have low CC (45-60%). Studies have revealed that uncontrolled content of oxygen and hydrogen play an important role in stabilizing the CC of magnesium alloys. Oxygen present in magnesium alloys in the form of suspended oxide inclusions changes the basic electrochemical properties of anodes. In open melting, the oxygen content (in terms of MgO) in magnesium melts is 0.001–0.02%. It has been established that the alloy components should contain less than 0.01% of oxygen to ensure maximum and stable CC. The solubility of hydrogen in the interaction with magnesium leaps in the transition of metal from liquid to solid state, contributing to the formation of gas porosity in the cast metal. The increase of hydrogen content in magnesium melts from 5 to 28 cm³/100 g leads to reduction of CC values from 1310–1340 to 1100–1260 A·hr/kg. A similar result was observed on the change of the magnesium alloys CC depending on the gas content. It is also established that the morphology of the crystalline structure of the cast sacrificial anodes has a significant influence on the stabilization of the magnesium alloys' CC. It is shown that the crushing of the cast structure of magnesium anodes from high purity alloys of the Mg-Al-Zn system provides not only maximum CC values but also reduces the spread of these values. Thus, in order to improve and stabilize the main electrochemical properties of the sacrificial anodes, technological processes have been developed that ensure in the process of the production of anodes the control of the required purity of melts on the maximum allowable content of cathodic impurities (Fe, Cu, Ni) and the restriction in the process of melting oxide inclusions and hydrogen with the mandatory conditions of casting, ensuring the grinding of the structure of cast anodes.

Key words: magnesium, compounds, impurities, structure, electrochemical properties.

Received: April 26, 2019. Published: August 8, 2019

doi: <u>10.17675/2305-6894-2019-8-3-10</u>

Introduction

Corrosion of metals leads to huge losses of both natural resources and material means. The annual loss of metals due to the corrosion is about 30% of their annual production, from them about 10% is lost irrevocably [1-8]. For protection against electrochemical corrosion of metal structures and constructions, cathodic protection systems with sacrificial magnesium, aluminum and zinc anodes became widely used. According to various countries, the use of this type or cathodic protection systems enhances the technical and economic performance of marine vessels, underground pipelines and other metal structures and structures, increases the service life and inter-repair periods of their operation. This corrosion protection technology reduces the thickness and mass of metal structures, decreases the labor intensity and cost of work related to the provision of corrosion protection means. The importance of protective protection increases even more with the increase of the network of trunk oil pipelines.

Efficiency of the practical use of protective materials for protection of metal structures from sea and soil corrosion depends on the sacrificial anodic alloy's specific properties and characteristics, availability and condition of paint coatings and insulating materials, temperature, composition and properties of the corrosive environment, and it is determined by the following criteria:

- Stability in time of the negative potential of sacrificial anodic alloys at wide modes of anodic polarization;
- High and stable actual current output, providing minimum possible non-productive losses of alloys and the longest life of the anodes;
- The minimum inclination of alloys to self-dissolution and the possibility of their effective use in combination with paint and insulating coatings;
- Optimum forms and sizes of anodes, providing the optimum value of a current, a surface area of a protective action and the specified service life of corrosion protection.

The most important indicators determining the efficiency and practical applicability of metals as the basis of sacrificial anodic alloys – materials (SAM) are their stationary (φ S) and working (φ P) potentials. Moreover, if the values of φ S approximate the possibility of using metal as the basis of the SAM, the values of the working potential give the final answer to this question. According to the basic criteria, the specific parameters and requirements to the SAM (material) taking into account the operating conditions, the use of aluminum, magnesium and zinc was found as the basis of the SAM. The basic physicochemical properties and electrochemical characteristics of metals-bases of SAM are given in Table 1.

It is known (Table 1) that magnesium has the most negative stationary potential compared to aluminum and zinc, which indicates its preference for use as the basis of protective alloys in low-conductivity corrosive environments, such as soil and some seas. However, comparison of values of theoretical and actual current output, determining the

coefficient of useful use of material of protectors, testify to the lowest values of CC for magnesium, then for other metals-bases of protective alloys.

Indic	ators	Al	Mg	Zn
Atomi	c mass	27.0	24.3	65.4
Density	<i>v</i> , g/cm ³	2.70	1.74	7.10
Melting tem	perature, °C	650	658.8	419.5
Stationary potential	in sea water, $-\phi_S$, V	0.56 1.40		0.82
Current output, Q , A · hr/kg	Theoretical	2980	2200	820
	Actual	2500	1100	800
Current capa	city (CC), %	84	50	97

Table 1. Properties and average characteristics metal-bases of SAM.

The given information testifies to actuality of works connected with increase and stabilization of the magnesium alloys in the direction of search of new compositions of alloys with reduced content of cathode impurity elements, gases and non-metallic Inclusions, as well as by improving the technology of melting and casting, providing a homogeneous structure of metal.

Magnesium alloy compositions

It is well known that aluminum and zinc are used as the main alloying components in magnesium alloys [9-13]. The experience of using magnesium anode to protect metal structures from electrochemical corrosion shows that in operating conditions Mg-Al-Zn-Mn alloys, having close values of working potentials, differ significantly in their CC values (Table 2).

It should be noted that magnesium alloys have a significant variation of CC values (45–60%) operating conditions. As a result, the service life and economic efficiency of protective protection against corrosion of metal structures using magnesium alloys are unpredictable. For this reason, in order to ensure reliable operation of the equipment, periodic diagnostics of the protection system efficiency and timely restoration of the protectors is a prerequisite. It is obvious that the increase and stabilization of the magnesium alloy CC is an important technical and economic task.

Initial characteristics of magnesium sacrificial alloys

The research results of the basic electrochemical properties of binary (Figure 1) and ternary (Figure 2) alloys on the basis of magnesium, alloyed with aluminum and zinc are presented below.

Countries -	Alloying elements			Impurities, no more			CC,	-φ _{p,}	
	Al	Zn	Mn	Fe	Cu	Ni	%	mŶ	
Russia	5.0–7.0 7.5–9.0	2.0–8.0 2.0–3.0	0.15–0.50 0.15–0.50	0.003 0.03	0.004 0.10	0.001 0.01	60 40	1250 1300	
England	5.3–6.7 5.3–6.7	2.5–3.5 2.5–3.5	0.15 0.15	0.003 0.003	0.05 0.02	0.003 0.002	50 50	1300 1300	
Japan	5.3–6.7 5.3–6.7	2.5–3.5 2.5–3.5	0.15–0.60 0.15–0.60	0.003 0.03	0.02 0,05	0.001 0.003	55 45	1300 1300	
USA	5.3–6.7	2.5-3.5	0.15	0.03	0.02	0.002	50	1300	
Germany	5.8-6.2	2.8-3.2	0.3	0.003	0.006	Traces	55	1250	

Table 2. Chemical composition (%) and averaged electro-chemical characteristics of magnesium alloys.



Figure 1. Dependence of the main electrochemical properties of magnesium on the content of aluminum (a) and zinc (b).

The analysis of the given data testifies, that magnesium alloys in the field of investigated compositions have heterogeneous structure consisting of grains of a α -solid solution of aluminum and zinc in magnesium, intermetallic phases (Mg₄Al₃, Mg₃Al₂Zn₂) on grain boundaries (Figure 3).

It should be noted that the degree of heterogeneity of the structure can vary not only depending on the concentration in aluminum and zinc alloys, but also on the casting conditions influencing the structure of cast magnesium protectors. This can be explained by the non-predictable variation of the CC values (up to 15%), made of one alloy grade and even one melting [10].



Figure 2. The main electrochemical properties of magnesium alloys of the Mg–Al–Zn system are: a – stationary potential, mV; b – working potential, mV (at polarization of current of 5 mA/m²); c – theoretical current output (Q_T , A·hr/kg); d – actual current output (Q_A), A·h/kg; e – corrosion rate, mm/year; f – CC, %.

In addition to the main alloying magnesium elements (Al, Zn), the magnesium sacrificial alloys additionally include elements to enhance technological and mechanical properties while improving the electrochemical characteristics of materials [10, 14, 15].



Figure 3. Microstructure (x250) of magnesium alloy in a cast state.

The following are the results of the selection of alloying elements for magnesium, based on the comparison of the inclination of elements to fusion with magnesium, as well as a comparative study of the physical and electrochemical properties of precipitation products account of economic valuation and other characteristics [14]. To reduce their solubility in magnesium (%) during the formation the structure of α -solid solutions built a number of recommended elements: Cd (100), Pb (41.7), Sn (14.8), Al (12.7), Zn (8.4), Li (5.5), Mn (3.4), Ca (1.0), Ce (0.85), Si (0.12) for alloying magnesium.

Analysis of data on theoretical current and electrochemical potential of elements allowed to leave in the group alloying for magnesium alloys. The following elements: Al, Zn, Li, Mn, Ca, Ce, Si are known to have chemical heterogeneity within individual grains of cast metal is the cause of electrochemical heterogeneity. Due to the tendency to intracrystalline liquor, Ce, Ca, Si and Mn should be considered as auxiliary alloying elements capable of improving the individual characteristics of magnesium alloys. For example, Mn and Si contribute to the reduction of iron content in magnesium alloys and the grinding of metal grains. Despite the negligible solubility of titanium and zirconium in magnesium, especially in the solid state, they are introduced into the composition of alloys to reduce the content of iron impurity and the crushing of the cast structure [16–17]. Comparing the results of the selection of alloying magnesium elements using different approaches, it is established that the match is obtained by the following elements: Al, Zn, Mn, Si, Ca.

Chemical purity of magnesium alloys

Applied sacrificial anodic alloys, having sufficiently close concentrations of alloying components, differ in the content of cathode impurities. The content of metallic impurities, gases and non-metallic inclusions has a significant effect on the actual current output of magnesium alloys and, as a consequence, on the CC of cast magnesium anodes. Depending

on the content of cathodic impurities (Fe, Cu, Ni) there is a significant change in the actual current output of magnesium (Figure 4).



Figure 4. The effect of separate (a) and total (b) content of impurities (Ni, Cu, Fe) on the current output value of magnesium.

The above data indicates the need to limit the maximum permissible concentrations of iron, copper and nickel to 0.0035%, 0.005% and 0.001%, respectively. Excess of the contents of these metallic impurities leads to the reduction and dispersion of the CC of the alloys within 30-40%.

It was found out an important factor influencing the quality of magnesium alloys is their purity in the content of gas and non-metallic inclusions Figure 5.

According to the established data, the increase of chlorine-ion magnesium content (especially in the electrolytic method of magnesium production and magnesium alloys preparation using chloride salts) from 0.004 to 0.25% leads to a decrease in actual current output on 10% (Figure 5a). Increasing the content of hydrogen magnesium (hydrogen accounted for up to 90–95% of all dissolved gases) from 4.0 to 28 cm³/100 g Mg leads to a decrease in its current output from 1340 to 1200 A·hr/kg (Figure 5b).

Increased dispersion of values of actual current output when contained in magnesium chlorine-ion, 0.05% and hydrogen > 15 cm³/100 g. Metal is caused by uneven distribution of chlorides and formation of gas porosity in the cast alloy. The reduction of current output with the increase of chlorides and hydrogen content can be caused by two factors.

First of all, it can occur as a result of the increased activity of micropores in the formation of sites (foci) containing chlorides, and in the presence of micro-chlorine dependent on the content and distribution of hydrogen. Secondly, the reduction of current output can be caused by the reduction of sample density due to the presence of both chloride and micro-chlorine inclusions.



Figure 5. Effect of chloride (a) and hydrogen (b) content on the current output of magnesium.

Oxygen is to be attributed to the non-regulated by standards for magnesium protective impurities. In the magnesium melts oxygen is in the form of suspended oxide inclusions, but in solid magnesium it is in the form as independent phase. Oxide inclusions, changing physic-chemical, technological and mechanical properties, affect the change of electrochemical properties of magnesium. In the real conditions of magnesium and magnesium alloys, production contains of oxygen in terms of magnesium oxide constituting 0.001-0.020%, should be limited to 0.01%.

The presented data on the influence of the chemical purity of magnesium melts (the content of impurity elements) on the values of CC confirm the need to control the maximum permissible contents not only to regulated by standards components (Fe, Cu, Ni), but also non-regulated by standards of harmful impurities (chlorine-ion, hydrogen, magnesium oxide).

It is obvious, that for increasing and stabilization of CC it is necessary to use the high purity magnesium alloys with recommended (Table 3) maximum-permissible contents of Fe, Cu, Ni, Cl, O, H.

Structure of magnesium alloys

One of the reasons for the occurrence of electrochemical heterogeneity, defining the CC of magnesium anodes, is the degree of their structural heterogeneity. The following are the results of research of structure and CC of magnesium anodic alloy (containing 6.7% Al + 2.8% Zn + 0.3% Mn) in melted and thermal treated states. The influence of heat treatment on the structure of magnesium alloys was studied on the samples cast in metal form. Thermal treatment of samples was carried out in the muffle furnace. Before loading in the furnace magnesium samples were sealed in ampoules of heat-resistant glass "Pyrex", from which preliminary pumped air to the residual pressure of $1 \cdot 10^{-2}$ mmHg. It was find out that the aging of magnesium specimens at specified temperatures during 1-8 hours with

subsequent cooling in the air leads to a significant change in the type of the microstructure (Figure 6).

 Table 3. Content of harmful impurities (%) in magnesium and sacrificial anodic alloys (SAA) on its basis.

 SAA

Impurities in the original magnesium		Russian standard	Suggestions for a group of impurities
		n	o more
Fe	0.03–0.05	0.003	0.003
Ni	0.001-0.002	0.001	0.001
Cu	0.002-0.02	0.004	0.005
Cl	0.001–0.5	_	0.005
O*	0.001-0.02	_	0.010
H**	3–25	_	15

Note: O^* – Oxygen content in terms of magnesium oxide; H^{**} – content of hydrogen, cm³/100g Mg.

It has been established that the heterogeneous structure (on the background of α -solid solution there are phases Mg₄Al₃ μ Mg₃Al₂Zn₂ typical for the cast state (a), depending on the temperature and duration of exposure goes to almost homogeneous structure (in the background). The dried α -solid solution Al and Zn in magnesium are visible remains of insoluble phases. The differences of the microstructure of the experimental composition of the alloy change the current output and the CC of magnesium specimens (Figure 7).



Figure 6. Microstructure (x100) of the magnesium alloy, depending on the heat treatment mode: alloy condition: cast (a); heat-treated shutter during 1–8 hours at 150 (b); 300 (c) and 500 (d) $^{\circ}$ C.



Figure 7. Change of the magnesium alloys current output \blacksquare and CC \blacksquare in seawater depending on the heat treatment (\square – value of scatter values of current output and CC). Alloy condition: cast (a) and heat treated during 8 hr. at 150 (b); 300 (c) and 500 (d) °C.

The effect of heat treatment on the standard modes on the structure of the metal is shown in Figure 8. It has been established that if annealing practically does not change the character of microstructure, hardening leads to dissolution of intermetallic phases (Mg₄Al₃, Mg₄Al₃Zn₃) with formation of homogenizing single-phase structures. Thermal treatment of aging causes the reverse separation of secondary phases, which are the products of decay of the transmitted metastable α -solid solution.



Figure 8. Microstructure (x100) of magnesium alloy depending on the heat treatment mode. The alloys conditions: a - cast heat-treated by modes: b - annealing, c - hardening, d - aging.

In Figure 9, the presented data on CC samples from magnesium alloy of the skilled composition, processed in various modes of heat treatment.



Figure 9. Influence of heat treatment and cooling speed of cast (a) and heat-treated modes: annealing (b), hardening (c) and aging (d) of magnesium alloy samples on CC in soil (1) and seawater (2).

It should be noted that the CC of alloys tested in soil is on average 3–5% higher than in seawater. In the Table 4 presented compositions and properties of high purity of Mg-Al-Zn sacrificial alloys, additionally containing Mn, Ti, Zr, and rare-earth metals (REM).

Different compositions of alloys on the basis of the Mg-Al-Zn system within the specified limits of alloying elements content practically do not affect the potential changes, CC and current output at polarization of current of 5 mA/m^2 .

Alloys	Al	Zn	Mn	Ti	Zr	REM*	Fe, no more	-φ _s , mV	СС, %	Q, A·hr/kg
1	5–7	2–4	0.15–0.5	—	_	_	0.004	1220	61	1340
2	5–7	2–4	0.02–0.5	0.001– 0.04	_	—	0.003	1220	65	1400
3	4–10	0.5–3.0	0.001 - 0.05	0.001– 0.05	_	_	0.003	1220	65	1400
4	5–10	2–4	0.15–0.5	_	0.005–0.2	—	0.003	1220	62	1380
5	5–10	2–4	0.15–0.5	—	—	0.005–0.2	0.005	1220	62	1380
6	9–10	2–4	0.1–0.5	_	0.005 - 0.02	_	0.003	1220	64	1390

Table 4. Composition (%) and average properties of magnesium alloys.

REM* – rare-earth metal

Different compositions of alloys on the basis of the Mg–Al–Zn system within the specified limits of alloying elements content practically do not affect the potential changes, CC and current output at polarization of current of 5 mA/m^2 . The introduction of manganese, titanium, zirconium and rare earth elements as microalloying additives provides a reduction in the content of iron impurity and contributes to the grinding of the structure of cast sacrificial materials. It has been established that additional microalloying contributes not only to the increase, but also to the stabilization of the CC of cast magnesium alloys in sea water. In addition, for all specimens, especially when tested in seawater, there is an increase in the CC with increased cooling speed of cast sacrificial anodes in the process of their manufacture from 35 to 500°C/min. Above this speed, alloys have a small-changing of CC.

Conclusions

- 1. The causes of electrochemical heterogeneity associated with the nature of the metal, composition and structure of the protective material have been established.
- 2. It is shown that the values of CC, which is the most important characteristics of protective magnesium alloys, depend on the chemical composition and purity of the material, as well as on the structure of sacrificial magnesium anodes.
- 3. In order to eliminate the scatter and stabilization of the values of sacrificial magnesium alloys, it is necessary to ensure not only the control of the maximum permissible contents of cathodic impurities (Fe, Cu, Ni), but also the control of the content in the alloys of ad-hoc by the standards of gases (hydrogen) and non-metallic inclusions (Cl-ion, magnesium oxide)-impurities.
- 4. It has been established that in the production of cast magnesium protectors it is necessary to provide conditions (melting, casting and heat treatment modes) to obtain a homogeneous structure of the metal, providing for all other equal conditions stable values of current capacity.

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