CORROSION BEHAVIOUR OF BINARY ULTRALIGHT MG-LI ALLOYS FOR PLASTIC FORMING

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Abstract

The paper outlines the course of corrosion processes in magnesium and Mg-Li alloys. The methodology of corrosion studies of alloys for plastic forming and their chemical composition as well as micrographs of alloys intended for research are presented.

Keywords: ultralight Mg-Li alloys, corrosion in alkaline and acid media

1. Introduction

The solubility of lithium in magnesium characterised by a hexagonal structure is low and amounts to about 5 wt%, while magnesium forms a wide range of the solid solutions β by dissolving in lithium of a regular bcc structure in an amount of up to 90 wt.%. Lithium is beneficial for the formability of magnesium alloys, replacing the hardly deformable hexagonal lattice of α-Mg (hcp) with a regular β-Li (bcc) lattice, resulting in a simultaneous drop of mechanical properties caused by the appearance of the β phase. An optimum combination of the alloy mechanical properties occurs in the two-phase α+β alloys containing 6-11 wt.% of lithium. Figure 1 shows the expected change in the density of Mg-Li alloy, depending on the chemical composition (mainly lithium content). The chart shows that it is even possible to obtain an alloy with a density of less than 1 g/cm^3. Alloys included in this family are capable of obtaining in as-cast state the elongation reaching even several dozen percent. An addition of aluminium to Mg-Li alloys [12] leads to the appearance in structure of a hexagonal δ phase representing the solid solution of Al in Mg with reduced deformability, a ductile λ phase, which is a solid solution of Al in Li of the bcc lattice, a hard - allowing the precipitation hardening – intermetallic Al-Li compound, and the η phase of B2 structure. The ductility of these alloys increases with the increasing content of δ+λ eutectic. Sometimes, a metastable Li$_2$MgAl phase may occur in these alloys, too [11].
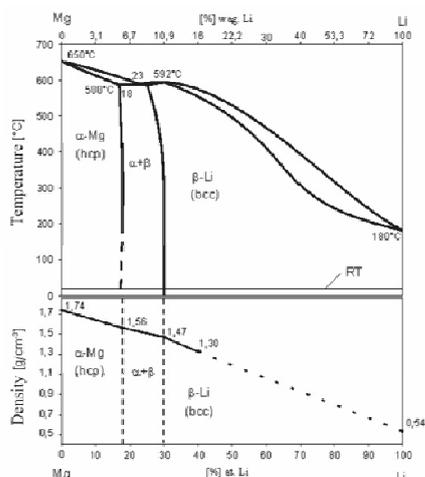

Fig. 1. Phase equilibrium diagram of Mg-Li alloys and change in alloy density with the changing Li content in a binary Mg-Li system acc. to [1]

Basically, the strength of Mg-Li alloys in as-cast state does not exceed 200 MPa, but certain additives such as Zn and Y, forming complex phases, may increase the strength of Mg-Li alloys up to about 450 MPa [13]. Magnesium, like most of its alloys of a hexagonal structure, has the cold deformability lower than aluminium alloys. In production practice, Mg-Al, Mg-Al-Zn and Mg-Mn are mainly used. At elevated temperature, the deformability of these alloys is higher. Ingot homogenisation reduces the yield point of the material, but formability remains low, which makes these alloys practically unsuitable for plastic forming. Even in the extrusion process, in which there is a positive state of stress, cracks appear in products, making low-speed extrusion necessary.

On the other hand, Mg-Li alloys subjected to plastic forming (mostly extrusion) show superplasticity. Some information on behaviour of these alloys is provided by ECAE process (Equal Channel Angular Extrusion) [9,14]. The ECAE process causes grain refinement in Mg-Li-Al alloys, an increase of mechanical properties and, for selected temperature and strain rate conditions, the elongation in tensile test can reach 300%.

Another reason for the limited technical use of these alloys is often their low resistance to corrosion, which results from the high reactivity of lithium. Yet, a systematic arrangement of the corrosion behaviour of Mg-Li alloys requires, first of all, discussing the fundamentals of corrosion of pure magnesium in aqueous solutions. As regards the corrosion of magnesium, the main problems is oxidation (redox reactions) during which the metal is oxidised by donation of electrons (partial anodic reaction), while in solution the reaction of reduction (partial cathodic reaction) takes place by uptake of electrons. During these reactions, depending on chemical composition of the solution, some specific types of corrosion occur, distinguishing in the corrosion mechanism between the hydrogen- and oxygen-induced corrosion [7, 8, 10].

In magnesium, the prevailing type is hydrogen corrosion and cathodic reaction (half-cell reaction). In this case, hydrogen ions act as an oxidising agent. As single processes of reaction, the following ones can be distinguished:
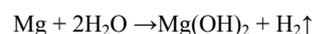
- partial anodic reaction (oxidising)

$$Mg \rightarrow Mg^{2+} + 2e^-$$

- partial cathodic reaction

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2\uparrow$$
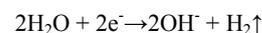
Hence, the equation for the overall reaction assumes the form of:

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2\uparrow$$

This type of reaction usually takes place in aqueous media, neutral or slightly alkaline, where the film of hydrated magnesium oxide is formed.

On this basis, the corrosion behaviour of magnesium-lithium alloys can be assessed in a more accurate way, conducting immersion tests under short-term loading and measuring the current density potential.

Additions of alloying elements such as lithium, aluminium and calcium have an impact on various corrosion mechanisms and phenomena taking place in magnesium alloys. Some ultralight alloys from the Mg-Li group are characterised by higher corrosion resistance than magnesium alloys used so far. For example, an Mg-12at.% Li alloy has a resistance to atmospheric corrosion higher than magnesium alone. An addition of calcium improves the corrosion resistance in the medium of synthetic seawater. Lithium as an alloying addition does not react with OH groups irrespective of the pH value. Owing to this, an outer layer of Mg (OH)$_2$ stabilised by increased pH value of lithium, is formed [10].

Analysis of literature [2-6] and own research conducted at the Foundry Research Institute and at the AGH Department of Non-Ferrous Metals indicate that the as-cast mechanical properties of Mg-Li alloys are relatively low, which limits their practical use. However, subjected to plastic forming, these alloys show a huge potential as regards the opportunities of obtaining a growth in both mechanical and plastic properties. Therefore, undertaking a research on Mg-Li alloys for plastic forming is expected to help in determining the possibility of their use in the manufacture of components, which are required to offer the smallest possible weight and high mechanical and plastic properties, e.g. in ground and air transport. There is also a need for basic research of the corrosion behaviour of these alloys in both as-cast state and after plastic forming.

2. Alloys for plastic forming and corrosion tests

Alloys were obtained using an experimental stand for melting and casting under controlled protective atmosphere [5,6] and pure ingredients such as magnesium and lithium, where lithium was in the form of pellets and ribbons. Three base alloys were selected for studies (according to the phase equilibrium system - see Fig. 1), i.e. alloy no.1 containing lithium at a level of 3-4 wt.% with the expected structure of α hcp, alloy no. 2 containing lithium at a level of 7-9 wt.% with the expected structure of $\alpha+ \beta$, and alloy no. 3 containing lithium at a level above 11% with the expected structure of β bcc.

Tables 1, 2 and 3 show the results of chemical analysis (GDS 850A optical spectrometer made by Leco) obtained on ultralight Mg-Li alloy. The chemical composition of the obtained alloys is consistent with the assumptions, and alloys will be subjected to corrosion tests and further plastic working under laboratory conditions of the AGH Department of Non-Ferrous Metals.

Table 1. Chemical analysis of alloy no. **1**
(monophase α hcp alloy; spectral analysis)

Designation						
	Li	Mn	Gd	Ni	Zn	Mg
Alloy 1 Sample 1 (1.1)	3,54	0,008	0,027	0,0131	0,002	Rest
Alloy 1 Sample 2 (1.2)	3,79	-	0,02	0,0142	0,03	Rest
Alloy 1 Sample 3 (1.3)	3,52	-	0,02	0,0143	0,02	Rest

Table 2. Chemical analysis of alloy no. **2**
(two-phase $\alpha+ \beta$ alloy, spectral analysis)

Designation	Chemical composition [wt.%]					
	Li	Mn	Gd	Ni	Zn	Mg
Alloy 2 Sample 1 (2.1)	8,15	0,0213	0,024	0,021	0,026	Rest
Alloy 2 Sample 2 (2.2)	8,07	0,0260	0,098	0,059	0,072	Rest

The determination by spectrographic method of lithium content in a monophase β alloy with relatively high lithium content (over 11%) was non-conclusive. The repeated measurements gave results differing by several percent. Therefore, for this alloy, a more precise method was a wet analysis. The results of the „wet" measurements are given in Table 3.

Table 3. Chemical analysis of alloy no. **3**
(monophase β bcc alloy, wet analysis)

Designation	Chemical composition [wt.%]	
	Li	Mg
Alloy 3 Sample 1 (3.1)	13,9	Rest
Alloy 3 Sample 2 (3.2)	14,1	Rest

Applying the atmosphere of protective gas, the obtained alloys were cast in metal moulds (dies) into ϕ50x50 mm and ϕ 12x100 mm ingots for further plastic forming. From these ingots specimens were cut out for metallographic examinations. Because of strong reactivity of alloys of this type, preparation of metallographic specimens required the development of special methodology. Magnesium alloys are very plastic, which naturally must create serious technical problems with proper preparation of polished sections. Microscopic observations and photographs were taken using a Neophot 32 metallographic microscope and metallographic polished sections were prepared in accordance with the instruction no. TBM/001. Samples were etched in Mi1Al reagent (acc. to PN-75/H-04512) and viewed in polarised light. The following figures show microstructures obtained in Mg-Li alloys cast in metal moulds. Specimens of these alloys were subjected to microstructural examinations in a laboratory of the Foundry Research Institute in Krakow.

Figures 2-4 show examples of microstructures of ultralight Mg-Li alloys, i.e. alloy **1** containing 3,54% Li (monophase α hcp alloy), alloy **2** containing 8.15% Li (two-phase alloy with α phase and $\alpha+\beta$ eutectic), and alloy **3**, containing about 13.9% Li (monophase β bcc alloy).

Fig.2. Microstructure of alloy **1**, etched in
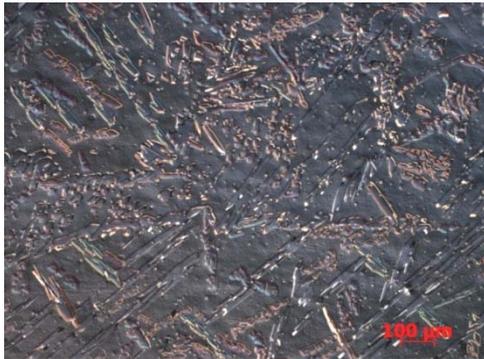Mi1Fe, phase contrast, 100x; visible is α–Mg–Li phase

Fig. 3. Microstructure of alloy **2**,
etched in Mi1Fe, phase contrast, 100x; visible is β phase
and α+βeutectic

Fig. 4. Microstructure of alloy **3**, etched in Mi1Fe,
polarised light, 12,5x; visible isβ-Mg-Li phase

3. Method to test the corrosion behaviour of Mg-Li alloys

Laboratory tests of corrosion behaviour of Mg-Li alloys were carried out by immersion at ambient temperature, based on standards: PN-76/H-04601, PN-78/H04610, BS EN ISO 16151. The principle of the method consisted in subjecting the samples of Mg-Li alloys to the effect of solutions prepared in the laboratory. The duration of individual measurement cycles was 6 h, 24 h, 48 h, 72 h and 144 h. Two series of tests were made at ambient temperature.

In series I, the immersion test was conducted in 5% aqueous solution of NaCl. To prepare the above solutions, analytically pure chemical reagents and redistilled water were used.

The object of corrosion studies were samples of Mg-Li alloys in as-cast condition of 30 x 20 x 10 mm dimensions.

The provided alloy samples were degreased by immersion in gasoline for 60 seconds, then they were washed with ethanol, dried and weighed. The prepared samples were tested for corrosion resistance by immersing them in a 5% aqueous solution of NaCl

and 5% aqueous solution of HCl for 6, 24, 48, 72 and 144 hours. The distance between the upper specimen edge and the mirror of the liquid was 35 mm. The volume ratio of solutions (NaCl and HCl) to the surface of the examined samples was 11:1. The samples were suspended in a solution using an insulating material neutral in respect of the examined alloy and the applied solution. Beakers with the immersed samples were placed in an empty desiccator. After the prescribed lapse of time, samples were each time washed with distilled water, immersed in ethanol for 30 seconds, dried and weighed. In studies, the density of the solutions used and their volume were monitored.

The measured loss of the sample weight was basis for the determination of the specific corrosion-induced loss of weight K_m [mg/cm^2] calculated from the following equation:

$$K_m = \Delta m/A \qquad (1)$$

where:
$\Delta m = m_0 - m_1$
m_0 – sample weight before the test [mg],
m_1 – sample weight after the test conducted for time t [mg].
A – sample surface area in cm^2.

The rate of the corrosion-induced loss of weight V_m [mg/cm^2 / 24 hours] was calculated from the equation:

$$V_m = K_m/t \qquad (2)$$

where: t – the time of corrosion test.

4. Corrosion tests of Mg-Li alloys in alkaline medium

Samples of the examined alloys (3 samples from each melt) were subjected to corrosion tests in accordance with the adopted programme of research. Figures 1 and 2 show in graphic form the results of corrosion-induced weight loss and corrosion rate.
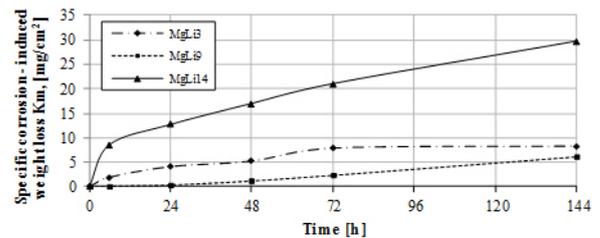

Fig 1. Comparison of the results of the corrosion-induced weight loss test carried out for Mg-Li alloys in 5% NaCl solution – specific corrosion-induced weight loss in time
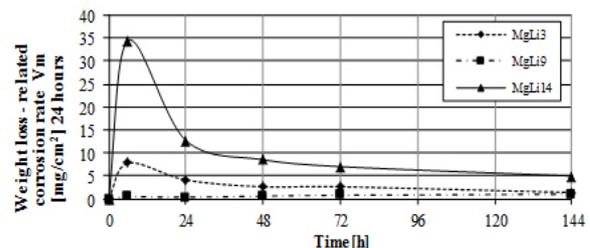

Fig 2. Comparison of the results of the corrosion-induced weight loss test carried out for Mg-Li alloys in 5% NaCl solution – weight loss-related corrosion rate Vm in time

Summary

Studies of the weight loss-related corrosion of Mg-Li alloys show an increase in the specific corrosion-induced weight loss K_m in time in the case of all the tested samples, the largest weight loss having been found in alloy with the highest content of lithium, i.e. in Mg-Li14 alloy (alloy no. 3), which is illustrated in Figure 1. The smallest weight loss was observed in a two-phase Mg-Li8 alloy (alloy no. 2). As results from Figure 2, the rate of the weight loss-related corrosion V_m for alloy no. 3, i.e. Mg-Li14, increased significantly in the first measuring cycle (6 h) and was 4.4 - fold higher than for alloy No.1. In subsequent measuring cycles (24 h, 48 h, 72 h, 144 h), the rate of the weight loss-related corrosion decreased for these alloys. On the other hand, in the case of the two-phase Mg-Li8 alloy, the weight loss-related corrosion rate increased slightly in the first measuring cycle (6 h), then slightly decreased after 24 h of the corrosive medium effect, to slightly increase again in the subsequent measuring cycles.

An analysis of the alloy sample surface showed that in alloy no. 1 (Mg-Li3,5) corrosion was spread evenly on the entire sample surface. The sample surface was coated with white, grainy bloom. The Mg-Li8 alloy showed evenly distributed corrosion, and the sample surface was covered with white, fine grains. In Mg-Li14 alloy, the corrosion was distributed unevenly, the surface was covered with black and white bloom. Numerous pits were also observed to occur.

It was noted that after a short time of being held in an aqueous solution of NaCl, the surface of pure magnesium was covered with a thin coating. An analysis of this coating showed that it was composed of rapidly combining MgO and $MgCl_2$. With prolonged exposure to the corrosive offect of an alkaline medium, the next bonds were formed giving MgH_2 and $Mg(0H)_2$. These coatings had a passivating effect, but the mechanism of their operation was not the same as in the case of aluminium, because they had relatively high porosity (pore volume) (MgO), or caused defects in the crystal lattice of Mg^2, leading to the formation of compressive stresses in the coating, finally threatening the coating detachment from the substrate. This phenomenon was particularly frequent in the case of $Mg(OH)_2$.

Summing up, it has to be stated that an increase in the lithium content in magnesium alloys from 3% to 9% increases the corrosion resistance of alloy (the lowest susceptibility to corrosion in NaCl solution showed the Mg-Li8 alloy). On the other hand, increasing the content of Li above 9% significantly increases the susceptibility to corrosion. These results allow concluding that the presence of lithium causes the formation of a thin film, which is more durable than pure magnesium and, considering the alkaline medium of corrosion, the coating is composed, at least partially, of LiCl. In the case of binary alloys with high lithium content, a rapid formation of the coating is observed, but it can be expected that starting with certain critical concentration of lithium, an intense reaction will proceed on the surface, while products of this reaction will not be capable of arresting further course of the reaction taking place between the metal surface and the corrosive medium.

In addition to the formation of a coating, which is considered a type of surface corrosion, a local corrosion occurs, too. These corrosion phenomena observed at a macro level on the surface can be qualified, first of all, as a pitting or intergranular corrosion. Local corrosion phenomena can be associated with precipitation effect as well as other types of effects such as a heterogeneous structure, which may be due to different electrochemical potentials of the structural constituentsm [2-6].

The observed local corrosion effects can be reduced by forming a homogeneous structure or by adding elements characterised by small difference of electrochemical potentials compared with the base binary alloy.

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