Corrosion behaviour of binary 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

Among the light metal alloys, magnesium alloys with lithium have the lowest specific weight. The density of these very lightweight (ultralight) alloys varies between 1.3 and 1.5 g/cm^3, which in the case of their use contributes to the reduction of the mass of components by about 25% compared with conventional magnesium alloys. A characteristic feature of these alloys is high rigidity and good deformability, which also occurs at low temperatures. So far, however, magnesium alloys with lithium have not been very popular in common use, although scarce cases of their practical application could be indicated. What accounts for this situation are rather poor mechanical properties in as-cast state and strong tendency to corrosion of these alloys [10].

Of great technical importance are magnesium alloys with aluminium, zinc and manganese, where Al and Zn increase the alloy strength, and Mn improves the corrosion behaviour. The alloying additives that increase their resistance to high temperatures and improve their plastic properties as well as oxidation resistance are: beryllium, calcium, cerium, cadmium, titanium. Iron, silicon and nickel lower the mechanical properties of alloys and their corrosion resistance. Magnesium alloys are characterised by a preferred ratio of strength and / or modulus to density, which makes them capable of carrying both static and dynamic loads similar to iron and aluminium alloys, and also have good damping properties. They are resistant to corrosion (provided pollutants like iron, nickel and copper are kept within a reasonable limit), and are resistant to changing mechanical loads, even under the conditions of elevated temperature. In addition to the well-known standard alloys based on Mg-Al-Zn and Mg-Al-Mn systems, used mainly in die casting technology, other alloys of fine-grained structure with an addition of zirconium are also available; they are characterised by increased creep resistance and are mainly designed for casting in ceramic moulds and gravity poured dies, and for processing by other methods. Magnesium alloys are used in construction of engine blocks, heads, gearbox housings, suspension components, steering parts, seats, body parts and other car accessories. These alloys are also used in the construction of motorcycles, in bicycles, sports facilities, recreational facilities, in the production of household appliances, etc. Magnesium alloys are successfully used in the aerospace industry (construction and helicopter airframe components) and for parts of electronic equipment (laptop cases, mobile phone parts, mainly due to, among others, their ability to absorb and scatter the electromagnetic radiation), in devices such as nuclear reactors for guards to absorb neutrons. Magnesium alloy castings are by 20-30% lighter than cast aluminium alloys and by 50-75%

lighter than cast iron alloys. Cast elements are made mainly by pressure die casting technology (approximately 90%)

Studies on Mg alloys are carried out to explore, e.g. possible use of alternative elements forming intermetallic phases, such as calcium, scandium, or gadolinium, which enhance the strength of the alloy at high temperatures. Particular attention deserve alloys with the addition of rare earth metals, and with the addition of yttrium and silver. For special applications in aerospace and sports cars, during short periods of time, they can withstand temperatures up to 300°C [12,13] offering, besides good resistance to high temperature, also adequate stiffness and wear resistance.

The newly developed composite materials based on Mg alloys reinforced with fibres and particles open the way for other uses for parts operating under the conditions of high and variable loads. Amorphous materials based on magnesium, still at the initial phase of basic research, are also worth mentioning. Widening the scope of research on their properties is in close relation with the development of innovative technological processes. In addition to improvements introduced to the processes already existing and used (e.g. pressure die casting, gravity die casting, etc.), new casting technologies are developed, such as semi-solid metal casting, squeeze casting, etc. Current development trends in the rapid crystallisation methods, spray casting method, and atomised dispersion of inert particles with a reactive introduction of alloying elements in situ offer further opportunities for the production of special magnesium alloys. In addition, metallic foams are a new-generation solution for the manufacture of ultra-light structural components.

Another use of magnesium are metallurgical processes, e.g. spheroidising treatment of cast iron and deoxidising of metal melt.

In recent years, a marked increase has been observed in the interest in magnesium and lithium alloys with additions of Al, Cd, Zn and Ag, characterised by a reduced density. It is assumed that 1 wt.% of lithium reduces the density of magnesium alloys by about 3%. Figure 1 shows the equilibrium phase diagram of Mg-Li alloys and the expected change in alloy density with change in the lithium content.

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/cm³. 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 [16] 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 Li₂MgAl phase may occur in these alloys, too [11].
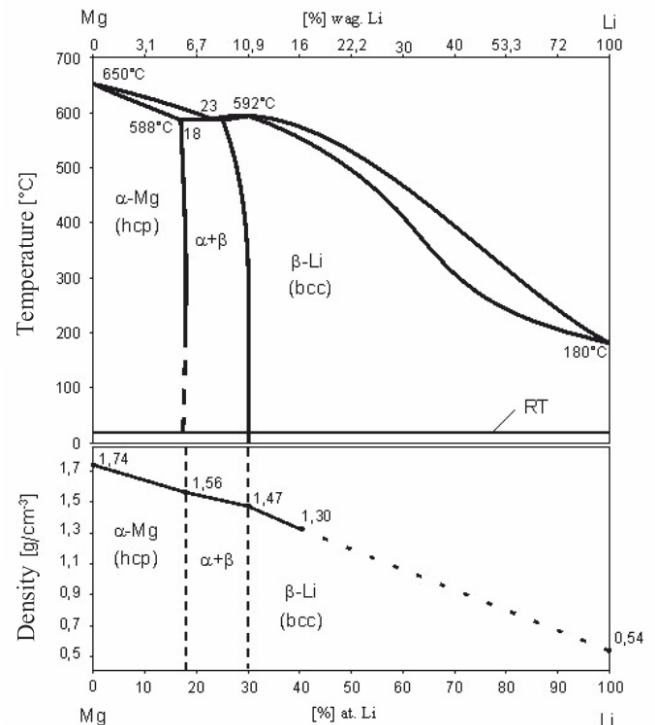

Fig. 1. Phase equilibrium diagram of Mg-Li alloys and change in alloy density with the changing Li content in a binary Mg-Li system acc. to [1]

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 [18]. 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:
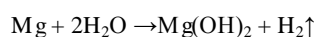
- partial anodic reaction (oxidising)

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

- partial cathodic reaction

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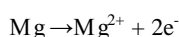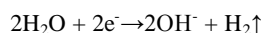
Hence, the equation for the overall reaction assumes the form of:

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

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].

Additions of Al and Ca increase the mechanical and chemical stability of Mg (OH)$_2$. Mg-Al alloys are generally perceived as a material stable in corrosive media and resistant to corrosion under natural conditions. Aluminium forms with magnesium a solid solution, which acts as a protective film in the form of a MgAl$_2$O$_4$ compound. Overvoltage also provides some protection. Another explanation for this phenomenon may be significant reduction of the difference in corrosion potentials, due to the presence of oxide-forming elements. However, a large addition of aluminium, e.g. in the order of 8 at.%, promotes selective corrosion in a multiphase structure. In inert environments, aluminium can be protected by the movement of Al$_2$O$_3$ on magnesium surface.

Calcium is used for the same reason as Li, i.e. owing to the formation with magnesium of a solid solution containing Ca and lack of reactivity with OH [7, 8]. Both these additives can form protective layers with Mg (OH)$_2$, which confer to the ternary magnesium alloys of Mg-Li-Al and Mg-Li-Ca type, the required corrosion resistance while maintaining high plastic properties and resistance to creep.

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 α+ β, 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 2-7 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).
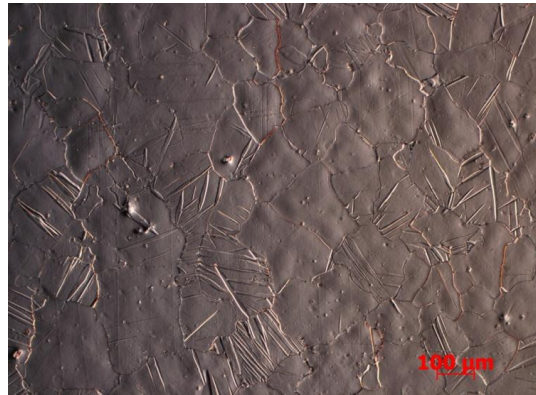

Fig. 2. Microstructure of alloy **1**, etched in Mi1Fe, phase contrast, 100x; visible is α–Mg–Li phase

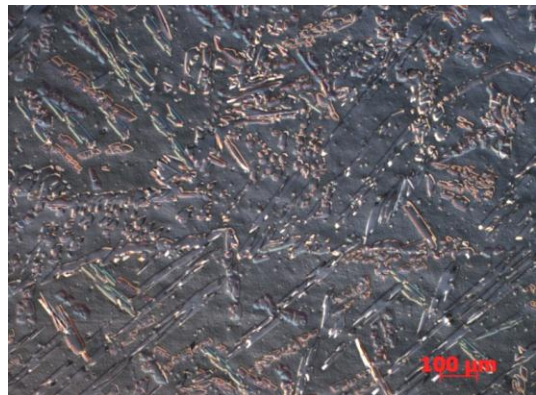Fig. 3. Microstructure of alloy **1**, etched in Mi1Fe, phase contrast, 200x; visible is α–Mg–Li phase
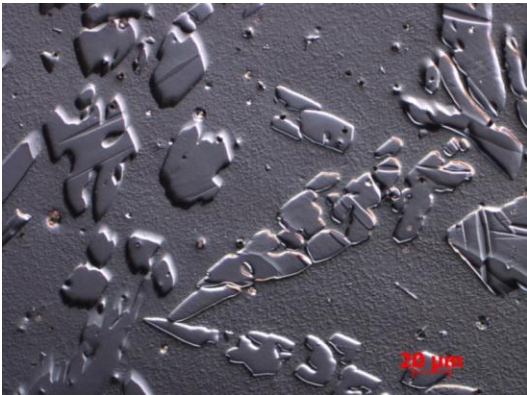

Fig. 4. Microstructure of alloy **2**, etched in Mi1Fe, phase contrast, 100x; visible is β phase and $\alpha+\beta$ eutectic

Fig. 5. Microstructure of alloy **2**, etched in Mi1Fe, phase contrast, 500x; visible is βphase and α+β eutectic
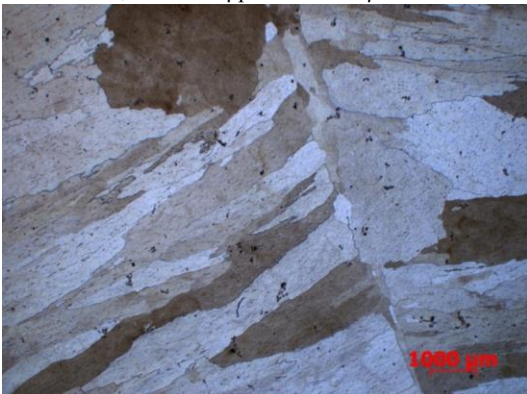

Fig. 6. Microstructure of alloy **3**, etched in Mi1Fe, polarised light, 12,5x; visible isβ-Mg-Li phase

Fig. 7. Microstructure of alloy **3**, etched inMi1Fe, polarised light, 50x; visible is β-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, while in series II the corrosive environment was 5% aqueous solution of HCl. 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 (Fig. 8) designated as:

— alloy no. **1** containing 3,54% Li (monophase α hcp alloy),
— alloy no. **2** containing 8,15% Li (two-phase alloy; β phase and α+β eutectic),alloy no. **3** containing about 13,9% Li (monophase β bcc alloy).

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.
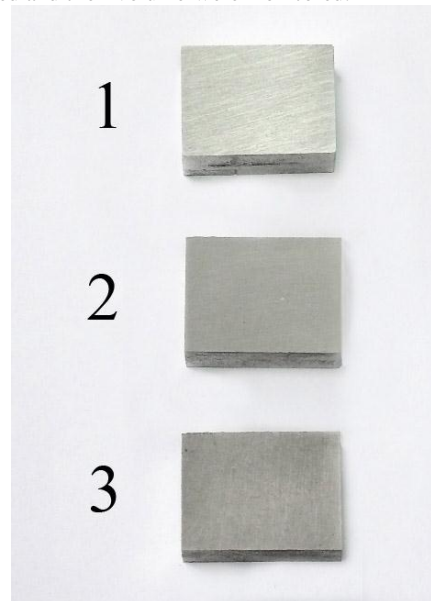

Fig. 8. Samples of the examined Mg-Li alloys in base state

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. Summary

The information presented and the discussed method of corrosion testing of Mg-Li alloys will be used for further study of ultralight Mg-Li alloys, both as-cast and after plastic forming.

Acknowledgements

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