

EFFECT OF ALLOYING ON THE CORROSION PERFORMANCE OF AS-ROLLED Mg-4Li ALLOYS (添加合金元素对轧制态 Mg-4Li 合金耐蚀性能的影响)

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Abstract: Mg-4Li alloys with the addition of Al, Si, Y elements were prepared by vacuum melting and rolling process. The microstructure, electrochemical corrosion of the alloys are investigated. The results indicate that the grain size and the second phase are modulated with the addition of Al and Y elements compared with the Mg-4Li alloy, the corrosion resistance is enhanced significantly. However, the Si element is detrimental to corrosion resistance, attributing to the more negative potential of Mg₂Si phase. The oxidation product primarily consist of Mg(OH)₂ and Li₂CO₃, which protected the Mg-4Li-3Al-1Si-0.5Y alloy effectively.

Keywords: Mg-Li alloys; Composition optimization; Microstructure; Corrosion behavior.

摘要: 通过真空熔炼和轧制工艺制备了添加了 Al、Si、Y 元素的轧制态 Mg-4Li 合金。研究了合金微观结构、静态腐蚀和电化学腐蚀等方面的区别。结果表明,随着 Al 和 Y 元素的加入,通过细化晶粒和调控第二相。合金耐蚀性得到了显著提高。然而, Si 元素对腐蚀是不利的,这归因于 Mg₂Si 相的电位较负,而 Si 是以共晶相的形式存在。Mg-4Li-3Al-1Si-0.5Y 合金的平均腐蚀速率为 15.71mm/年。氧化产物膜主要由 Mg(OH)₂ 和 Li₂CO₃ 组成,有效地保护了基体。

关键词: Mg-Li 合金; 合金化; 电化学; 腐蚀行为

1. Results and discussion

1.1 As-rolled microstructures observation and phase analysis

The α -Mg grains are rolled into thin strips and short rods. The α -Mg phase in the L4 alloy becomes significantly elongated, and the grain size of the LA43 alloy is refined, the number of precipitated phases increases significantly. The white β -Mg₁₇Al₁₂ phase precipitates along the grain boundaries, which is diffusely distributed in the α -Mg matrix. LASW4310 alloy has α -Mg phase, MgLi₂Al phase, AlLi phase, Mg₁₇Al₁₂ phase, Mg₂Si phase. The addition of 0.5 wt.% Y increases the number of fine white particles in the alloy, which is consisted of Mg₂₄Y₅ phase and is distributed along the rolling direction. Meanwhile, the LASW4310 alloy grains are notably refined. This suggests that the performance of the alloy is enhanced by fine grain strengthening and dispersion strengthening.

1.2 Static corrosion

The LASW4310 alloy is immersed in 3.5 wt.% NaCl solution for 24 h. The corrosion product film is tested by XPS. In general, alloys containing rare earth elements will naturally form rare earth oxide surface film after a period contact with air, which has a positive impact on the corrosion resistance. The formation of surface films is independent on micro-electro-couple corrosion and depends only on the composition and structure of alloys. Figure (a) presents the full XPS spectrum of the oxide film formed in the aqueous NaCl solution. Diffraction peaks of the elements Mg, O, C, Al, Li were completely detected. Obviously, the diffraction peaks of the alloy elements Al and Li were weak in intensity, indicating their relatively low elemental content. By precise measurement, the corrosion product layer of LASW4310 alloy are largely comprised of Mg(OH)₂.

The Pilling-Bedworth ratio (PBR) is usually used to reflect the stress condition in the oxide film. Compared with the high chemical activity of Li, the formation of Li₂CO₃ depends on low standard enthalpy. The oxide film, formed on the HCP-structured Mg-Li alloys surface, mainly consists of Mg(OH)₂ and Li₂CO₃. The Li₂CO₃ formed has a PBR value of 1.35, which can efficiently inhibit the occurrence of pitting corrosion. The PBR value of Mg(OH)₂ is 1.77, which could effectively protect the α -Mg phase during the initial stage of corrosion.

1.3 Electrochemical tests

The open-circuit potential is the steady-state self-corrosion potential of the alloy without applied current, consequences are given in Figure. Briefly, the more negative the steady-state self-corrosion potential, the greater the tendency for electrochemical corrosion to occur. Throughout the testing process, the self-corrosion potentials do not change drastically and the distinction is not evident yet. In other words, the dynamic equilibrium is established between the generation and dissolution of the corrosion product film, making the open-circuit potential nearly at stable values.

The kinetic potential polarization curves reflect the instantaneous polarization response of the alloys, and the corresponding results are exhibited in Figure. In the kinetic potential polarization curves, the cathodic branch usually represents hydrogen precipitation. In contrast, the anodic branch usually indicates the dissolution of the substrate. There is no obvious fluctuation in the cathodic branch, demonstrating that there is no obvious fluctuation in the hydrogen precipitation rate. The corrosion rate is constant, which is consistent with previous open circuit potential test results.

The electrochemical impedance spectra are displayed in Figure. There exist high-frequency capacitive-resistance arcs and low-frequency inductive-resistance arcs with large radii. Usually, alloys of different types and states have various corrosion mechanisms. In general, the generation of high-frequency capacitive arcs is associated with double-layer charge transfer between alloy surface and electrolyte surface. The presence of low-frequency inductive resistance arcs implies that mass transfer of ions occurs in the loose and porous corrosion product layer.

The Bode phase angle diagram and impedance modal diagram are fitted using ZSimpWin software. LASW4310 alloy has the largest phase angle peak and the broadest peak width. This alloy has larger resistance, smaller capacitance and the slowest corrosion rate. The impedance modulus Z_{mod} for the experimental alloys is in the following order: LASW4310>LAS431>LA43>L4. The greatest polarization resistance represents the alloy with the best corrosion resistance. Bode plot results are consistent with the Nyquist curve above.

1.4 The activation energy of alloys

Generally, the activation energy (E_a) represents the resistance to the reaction. The higher the activation energy, the more difficult the reaction. The magnitude of the activation energy for different alloys can be determined from the following Arrhenius equation:

$$\ln I_{corr} = -\frac{E_a}{R \times T} + \ln A.$$

The I_{corr} of the alloy has been measured in kinetic potential corrosion experiments. The order of magnitude of the activation energy E_a for different alloys is LASW4310 > LA43 > LAS431 > L4.

2. Effect of alloying elements on Mg-4Li alloy corrosion resistance

The addition of Al can increase the hydrogen precipitation overpotential. At the same time, it can also make the surface film of Mg-Li alloy containing aluminum and promote the formation of a more stable $Mg(OH)_2$ protective layer. $Mg_{17}Al_{12}$ compounds are formed in Mg-Li alloys in media with high ion concentrations (especially Cl^-). $Mg_{17}Al_{12}$ has two distinct effects on the corrosion process. It plays a role as a barrier to hinder the corrosion of Mg-Li alloys. From another aspect, it forms a corrosion cell with the matrix and acts as a cathode, accelerating the corrosion rate. Clearly, the former has a stronger role than the latter. Thus, the corrosion resistance of LA43 is significantly superior to that of L4 alloy.

The LAS431 alloy mainly contains the Mg_2Si phase. In the early stages of corrosion, Mg_2Si acts as an anode for dissolution, which can be attributed to the more negative potential than the matrix. Pitting pits or intergranular corrosion cracks can be observed on the alloy surface. A point of interest is that Mg in the Mg_2Si phase is preferentially dissolved in the process of anodic dissolution. Si was also present as a eutectic phase, which can be easily dislodged due to partial etching of the magnesium matrix in the vicinity of the Si phase.

The rare earth compounds have a pegging influence on the dislocation organization of the alloy and will reduce the number of corrosion pits generated due to the hydrogen precipitation

process. It also reduces the amount of non-rare earth compounds in the Mg-Li alloy, reducing the cathode for micro-electro-couple corrosion. Y element makes the surface film of Mg-Li alloy denser, due to the reaction with oxygen can generate a discontinuous passivation protective film. The precipitated compounds containing Y are distributed near the phase boundaries and act as sacrificial anodes. To sum up, these greatly intensify the corrosion resistance of Mg-4Li alloy.

1. 引言

煤炭、石油等燃料的大量使用，带来了众多环境问题，比如温室效应、雾霾等。与此同时，化石燃料资源枯竭，也是未来所要面临的棘手问题。人们愈加注重新能源的研发，希望绿色环保、高效的新能源能够在能源领域发挥重要作用。镁-空气电池已经突破了一些技术壁垒，很好地继承了燃料电池的优点。其成本低廉、绿色无污染、性能高效、安全可靠，并且属于可再生能源[1]。但是作为镁-空气电池的核心部件，阳极材料自腐蚀速率过快以及放电话性被抑制等问题一直亟待解决[2]。利用加入合金元素的方式制备阳极材料，是提升镁-空气电池材料性能的有效手段。

许多研究已经证实，添加合金元素，特别是稀土元素，是一种简单而有效的提高耐腐蚀性的方法。Al 元素可以增加氢过电位，抑制剥落腐蚀，并提供致密的 $Mg(OH)_2/Al$ 氧化膜以防止更深的腐蚀。稀土元素 Y 可以有效地抑制腐蚀。生成具有高熔点的金属间化合物，使其具有更好的机械性能和耐腐蚀性[3]。此外，在中性电解质中形成稳定的 $Y(OH)_3$ 薄膜。钇 (Y) 和镁的标准电化学电位是相同的 (-2.372 V)，表明 Y 元素溶解在 Mg 基体中，不会引起微电耦合腐蚀。相关化合物较低的电极电位降低了第二相与基体之间的腐蚀驱动力，可以明显减弱微电耦腐蚀[4]。

通过实验制备了含有不同合金元素的轧态 Mg-Li 合金。对合金元素的作用和腐蚀机制进行了全面的分析，并对合金进行放电性能测试。为避免赘述，下文的实验合金默认为轧态。

2. 结果与讨论

2.1 微观组织与相分析

轧制后的微观结构及其能谱分析，再结合 XRD 结果可见。合金中的 α -Mg 晶粒被轧制成细条和短棒。L4 合金中的 α -Mg 相明显变长，而 LA43 合金不仅被细化，而且析出相的数量也明显增加。白色的 β - $Mg_{17}Al_{12}$ 相沿晶界析出，在 α -Mg 基体中弥散分布。LASW4310 合金有 α -Mg 相， $MgLi_2Al$ 相， $AlLi$ 相， $Mg_{17}Al_{12}$ 相， Mg_2Si 相。加入 0.5wt.% 的 Y 会增加合金中白色细小颗粒的数量。它由 $Mg_{24}Y_5$ 相组成，沿轧制方向分布。同时，LASW4310 合金的晶粒明显细化。这表明，合金的性能通过细晶强化和弥散强化得到了提高。

2.1 静态腐蚀

LASW4310 合金在 3.5wt.% NaCl 溶液中浸泡 24 小时。用 XPS 测试腐蚀产物膜。一般来说，在空气中放置一段时间后，含有稀土元素的合金会自然形成含有稀土的氧化膜，这对耐蚀性有积极影响[8]。表面膜的形成与微电偶腐蚀无关，只取决于合金的成分和结构。在 NaCl 溶液中形成的氧化膜的完整 XPS 光谱中。Mg、O、C、Al、Li 等元素的衍射峰被完全检测到。很明显，合金元素 Al 和 Li 的衍射峰强度较弱，表明其元素含量相对较低。通过精确测量，LASW4310 合金的腐蚀产物层主要包括 $Mg(OH)_2$ 和 Li_2CO_3 。

我们通常使用 Pilling-Bedworth ratio (PBR) 来反映氧化膜的应力状况。PBR 是合金表面金属离子和原子的体积比。当 PBR 值在 1 到 2 之间时，表面氧化膜中会产生压应力。这种氧化膜相对致密，金属对氧化/腐蚀有抵抗力；对于 PBR 值小于 1 或大于 2 的情况，会出现拉应力或过度的压应力。这种情况往往会导致薄膜破裂。因此，降低了金属的抗氧化性/腐蚀性。

与 Li 的高化学活性相比， Li_2CO_3 的形成取决于相当低的标准焓。在 HCP 结构的镁-锂合金表面形成的氧化膜主要由 $Mg(OH)_2$ 和 Li_2CO_3 组成。形成的 Li_2CO_3 的 PBR 值

为 1.35，可以有效地抑制点腐蚀的发生。 $Mg(OH)_2$ 的 PBR 值为 1.77，在腐蚀的初始阶段，它应该有效地保护 α -Mg 相。随着腐蚀时间的增加，Cl⁻溶解了较密集的 $Mg(OH)_2$ 保护膜，最终形成 $MgCl_2$ 。

2.3 电化学腐蚀

开路电位是指合金在没有外加电流情况下的稳态自腐蚀电位。简言之，稳态自腐蚀电位越负，发生电化学腐蚀的趋势就越大。在整个测试过程中，自腐蚀电位不会发生剧烈的变化，区别还不明显。换句话说，在腐蚀产物膜的生成和溶解之间建立了动态平衡，使开路电位几乎处于稳定值。

动电位极化曲线反映了合金的瞬时极化反应。在动电位极化曲线中，阴极分支通常代表氢气析出。相反，阳极分支通常表示基体的溶解。阴极分支没有明显的波动，意味着氢气析出速率没有明显的变化。腐蚀速率是恒定的，这与之前的开路电位测试结果一致。在图 11 中，自腐蚀电位和自腐蚀电流密度由 Tafel 拟合得出。 I_{corr} 值的大小代表了第二相和基体之间微电偶腐蚀驱动力的强度。 I_{corr} 值越大，合金的微电偶腐蚀驱动力越强，耐蚀性越差。L4 合金拥有最大的 I_{corr} 值，LA43 合金的 I_{corr} 值明显下降；然而，LAS431 合金的 I_{corr} 值反而略有增加。LASW4310 合金的 I_{corr} 值比较小，这意味着氢气析出的速率较慢，合金的耐腐蚀性较高。

在电化学阻抗谱 Niquist 图中，存在高频容抗弧和大半径的低频感抗弧。通常情况下，不同类型的合金有不同的腐蚀机制。一般来说，高频容抗弧的产生与合金表面和电解质表面之间的双层电荷转移有关。低频感抗弧的出现意味着在松散多孔的腐蚀产物层中发生大规模的离子转移。

使用 ZSimpWin 软件对 Bode 图进行了拟合。LASW4310 合金的相角峰值最大，峰宽最宽。这种合金的电阻较大，电容较小，腐蚀速率最慢。合金的阻抗模量 Z_{mod} 按以下顺序排列。LASW4310>LAS431>LA43>L4。最大的极化电阻代表合金具有最佳耐蚀性。Bode 图呈现的结果与上述 Nyquist 图一致。

2.4 合金的活化能

一般来说，活化能 (E_a) 代表反应的阻力。活化能越高，反应就越困难。不同合金的活化能的大小可以通过以下阿伦尼乌斯方程来确定：

$$\ln I_{corr} = -\frac{E_a}{R \times T} + \ln A.$$

合金的 I_{corr} 已经在动势腐蚀实验中被测量出来。不同合金的活化能 E_a 的数量级是 LASW4310 > LA43 > LAS431 > L4。

3. 结论

通过对不同元素含量的轧制态 Mg-4Li 合金的微观组织、静态腐蚀行为、电化学腐蚀行为的分析，可以得出以下结论：

- (1) 随着合金元素的加入，生成的 $Mg_{17}Al_{12}$ 、AlLi、 $Mg_{24}Y_5$ 相导致轧制态 Mg-4Li 合金晶粒尺寸明显减小，有利于合金耐蚀性的提高。
- (2) Mg-4Li-3Al-1Si-0.5Y 合金具有最佳的耐腐蚀性。在 3.5 wt.% NaCl 溶液浸泡一段时间后，产生的由 $Mg(OH)_2$ 和 Li_2CO_3 组成的相对密集的混合腐蚀产物膜，可以有效地保护基体。
- (3) 就轧制态 Mg-4Li 合金而言，Al 和 Y 元素凭借对合金晶粒的细化作用和对第二相的调控增强了合金耐蚀性。Si 元素稍微降低了耐腐蚀性， Mg_2Si 相与基体形成微电偶腐蚀，加速了腐蚀速率。