Reducing the corrosion rate of magnesium via microalloying additions of group 14 and 15 elements

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ABSTRACT

A characteristic of magnesium (Mg) dissolution is that dissolution is accompanied by a concomitant increase in the hydrogen evolution reaction (HER), a phenomenon known as cathodic activation. When magnesium undergoes free corrosion or forced dissolution in response to anodic polarisation, cathodic activation is manifest, which allows magnesium dissolution to readily proceed. However, recent work revealed that alloying magnesium with micro additions of arsenic, As (a group 15 element) was capable of retarding cathodic activation, resulting in a significant reduction in the corrosion rate of Mg-As alloys. As such, in the pursuit of elements with similar chemical and electrochemical properties to arsenic, but with less toxicity, a number of group 14 and 15 elements were alloyed with magnesium and reported herein. Based on the binary alloying additions studied herein, it was revealed that Bi, Ge, Pb, Sb and Sn, demonstrated suppression of cathodic activation of Mg following anodic polarisation (about one order of magnitude lower based on the cyclic galvanostatic-potentiostatic testing), in addition to lower free corrosion rates (about one order of magnitude based on the mass loss and hydrogen evolution testing). Employing a number of corrosion rate assessments, including online atomic emission spectroelectrochemistry, it was shown that reduction in Mg corrosion rates — historically considered difficult to achieve — can be robustly demonstrated. The present work has implications for the development of more corrosion resistant Mg alloys, Mg anodes for cathodic protection, or for the use of Mg as a primary battery electrode.

1. Introduction

Magnesium (Mg) and its alloys possess high specific strength, which makes them attractive structural materials for light-weighting [1–5]. To date, there is also substantial and growing interest in the utility of Mg as an electrode material in both primary and secondary battery systems, due to its high energy density [6,7]. As well recognised, the inherently high rate of Mg corrosion in aqueous environments restricts the wider engineering application of Mg [1,3,8]. The high dissolution rate of Mg anodes at open-circuit causes "parasitic discharge" issues in primary Mg battery systems [9–11]. Thus, using appropriate approaches for controlling the corrosion of Mg is of vital importance.

Compared to common engineering metals, Mg is highly reactive in aqueous environments [1,12]. Water reduction ($2H_2O + 2e^- \rightarrow H_2 + 2OH^-$) is the primary cathodic reaction which has few kinetic limitations, such as no requirement for the presence oxygen [13]. Magnesium itself is incapable of forming a passive surface oxide/hydroxide layer in aqueous or moist environments of pH < 11 [1,12,13], and consequently, corrosion of Mg occurs readily over a wide pH range (from about pH −2 to ~10.5) [12]. Furthermore, under anodic polarisation, the rate of partial cathodic reaction upon Mg, which is the hydrogen evolution reaction (HER), also increases substantially with increasing anodic potential. This phenomenon is termed the "negative difference effect (NDE)", which has been documented for several decades [14–19]. The recent works of Williams and co-workers described a so-called anodically induced "cathodic activation" phenomenon, which was clarified using the scanning vibrating electrode technique (SVET) [20,21]. The notion that cathodic (catalytic) activity is enhanced by prior anodic polarisation has also been confirmed in a variety of tests using conventional electrochemical methods [19]. In addition,

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cathodic activation of Mg has been found to occur in chloride containing electrolyte without any external polarisation [22]. The anodic reaction kinetics of Mg dissolution as assesses from potentiodynamic polarisation testing curve reveals a very low Tafel-slope, concomitant with the inherently non-polarisable nature of Mg [13]. As such, small changes in cathodic kinetics have a significant effect on the overall corrosion rate of Mg, and corrosion of Mg may be considered a "cathodic reaction controlled" process.

With respect to the control of Mg corrosion, either utilisation of surface protective coatings or appropriate alloying is required [23–26]. Corrosion protection of Mg by surface treatment incurs a significant cost in many cases, in addition to coatings on Mg being inherently restricted to barrier coatings that are unable to protect at defect sites. Consequently, corrosion resistant Mg alloys via alloying remain an attractive route. Unlike the improvement of mechanical properties by alloying, which is widely reported in the literature [2,27,28]; alloying additions generally increase the rate of cathodic reaction and anodically induced cathodic activation upon Mg, leading to more severe corrosion of Mg which has been documented in several reviews [15,29–31]. In comparison to other metals, Mg has an inherently poor ability to support a cathodic reaction (i.e., Mg itself has a low exchange current density for the HER) [32] and the presence of more noble alloying elements or second phases promotes intense localised cathodes that support HER at comparatively higher rates [33]. The limited solid solubility of a wide range of elements in Mg [24,27] restricts the use of appropriate alloying (to a critical concentration) required to modify the surface oxide layer properties. The exceptional case has been reported in the recent work of Xu et al. [34], wherein an Mg-10.9Li (wt.%) alloy with a body centred cubic (bcc) structure was developed. The Mg-Li alloy possessed a dynamically formed Li-rich carbonate surface film, which provided remarkable corrosion resistance [35]. However, imparting this stainless-like character to other Mg alloys with hexagonal close packed (hcp) structure via forming an inherently formed passive surface films as similar to Mg-Li alloy, is challenging [36]. Thus, the development of corrosion resistant Mg alloys via metallurgical alloying is indeed an aspect of important work.

A recent breakthrough in the development of an intrinsically corrosion resistant Mg alloy was achieved via the use of micro-alloying additions of arsenic (As) [37], to reduce cathodic kinetics and suppress cathodic activation, imparting remarkable corrosion resistance to Mg. However, the use of As is considered problematic in industrial manufacturing (or even laboratory testing) owing to the toxicity of As. Therefore, the pursuit of less toxic elements to control the corrosion of Mg in a manner similar to that demonstrated by Mg-As, would provide a practical corrosion control route. The corrosion protection imparted by the small concentration of metallic As relies on the ability of As species to serve as a poison for cathodic reaction and to hinder cathodic reaction and overall corrosion reaction of Mg [38,39]. In addition, cathodic poisons are capable of effectively retarding the rate of cathodic reaction at low concentrations [40,41]. In pursuit of elements that possess similar inherent catalytic traits with As, but with less toxicity, a number of group 14 and 15 elements including bismuth (Bi), germanium (Ge), lead (Pb), antimony (Sb), and tin (Sn) were studied herein [42,43].

There exist several reports regarding the influence of aforementioned group 14 and 15 elements on the corrosion of Mg and Mg alloys. It was reported by Tak et al. [44] that addition of Bi (0.5–15 wt%) deteriorated the corrosion resistance of Mg-1.2Ca alloy. The work of Zhou et al. [45] indicated that combined addition of 1.0 wt% Bi and 0.4 wt% Sb to AZ91 alloy resulted in more rapid corrosion. In the case of Ge, an early study by McDonald in 1942 [46] investigated a number of Mg binary alloys with Ge alloying additions (0.1–10 wt%). It was suggested that 0.5–5 wt% of

Ge was the optimum range to improve the yield and tensile strength of the alloys [46]. Recent work by Kim et al. [47] suggested that the corrosion rate of Mg-Ge binary alloys (0.5–2 wt%) was lower than pure Mg in 3.5% NaCl. The author hypothesised that Ge alloying was capable of refining grain structure and stabilising the surface film upon Mg, which contributed to the improvement of corrosion performance of Mg [47]. However, such a hypothesis was lacking any experimental evidence. It is also debatable that whether grain structure is the dominant factor on the corrosion of Mg alloys with heavy alloying loading and Ge alloying can affect the surface film stability [24,26,36]. Hanawalt et al., in 1942 [48], suggested that Pb additions did not deteriorate the corrosion of Mg-Pb alloys up to 5 wt%. The use of Pb alloying to produce Mg anode material has been studied by the works of Wang et al. [49–52] with Mg-6Al-5Pb (wt.%) and Mg-6Al-5Pb-1In (wt.%) alloys; reporting that the Pb containing alloys displayed more significant anodic reaction activity and subsequently demonstrated higher discharging current density output in the context of Mg battery. In another study by Cicek et al. [53], the corrosion resistance of Mg-10Al-12Si alloy (wt.%) was improved with Pb addition (0.2–1 wt%). Whilst, alloying AZ91 alloy with Pb addition was reported to have a negative effect on the corrosion resistance of the alloy [54]. As similar to Pb, the addition of Sb was also found to be detrimental for the corrosion of AZ91 alloy, which increased cathodic kinetics and led to a more rapid corrosion [54]. As for the case of Sn, Wang et al. [55,56] indicated that addition of Sn (1–3 wt%) to Mg-6Al-1Zn and Mg-6Al-5Pb-0.5Mn-0.5RE increased the anodic kinetics of the alloy. Song [57] reported that 2 wt% of Sn to Mg-7Al-0.2Mn (wt.%) alloy accelerated the anodic kinetics of the alloy. In the binary context, Gu et al. [58] indicated that the corrosion rate of Mg-1Sn (wt.%) was more rapid than pure Mg. Contradictorily, Ha et al. [59] described an extruded Mg-Sn alloy with a heavy Sn loading of 5 wt%, which displayed improved corrosion resistance in comparison to pure Mg.

The above-mentioned studies generally investigated the corrosion behaviour of Mg alloys with comparatively large alloy loadings of group 14 and 15 alloying elements –with such alloying either utilised as ternary or quaternary alloying additions. In such cases, the impact of the alloying may have been overwhelmed by the complex metallurgical reactions between the alloying additions and other elements (such as Mn and rare earth elements) present. Thus, the primitive influence of group 14 and 15 elements on the corrosion and more specifically, the cathodic reaction kinetics upon Mg, have not been unambiguously elucidated yet. One effort in this aspect has been demonstrated by a recent study by Liu et al. [60], where micro-alloying additions of Ge (0.1 wt% and 0.3 wt %) suppressed cathodic kinetics and cathodic activation of Mg, imparting a significant corrosion resistance to Mg.

The work herein was uniquely designed on the basis that the micro additions of group 14 and 15 elements (≤0.5 wt%) were used as a binary alloying addition to Mg, which rules out any possible complex (metallurgical) interactions with other elements in the alloy. The aim of this work is to comprehensively explore the possibility of micro-alloying the elements: Bi, Ge, Pb, Sb and Sn to serve as effective and less-toxic functional alloying additions, exploring a practical corrosion protection method for Mg. The influence of the elements on the catalytic activity of Mg towards HER will also be comprehensively assessed. Findings from prior investigation of Mg-Ge [60] are included in this work for comparison purpose.

2. Experimental methods

2.1. Materials

The custom produced Mg alloys reported herein were produced