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Short communication

A new concept for corrosion inhibition of magnesium: Suppression of iron re-deposition

S.V. Lamaka [a,*], D. Höche [a], R.P. Petrauskas [a,b], C. Blawert [a], M.L. Zheludkevich [a,c]

[a] MagIC—Magnesium Innovation Centre, Helmholtz-Zentrum Geesthacht, Max-Planck Str. 1, 21502 Geesthacht, Germany
[b] University of Vilnius, Department of Inorganic Chemistry, 03225 Vilnius, Lithuania
[c] University of Aviero, Department of Materials and Ceramic Engineering/CICECO, 3810-193 Aveiro, Portugal

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ABSTRACT

In our recent work (Höche et al. 2016) we proposed that non-faradaic dissolution of Fe impurities and/or iron containing phases with subsequent re-deposition of thin film of pure ("in statu nascendi") iron enlarges cathodically active sites at the surface of corroding magnesium. The effect drastically accelerates corrosion of impurity containing Mg. In the present work we assume that if Fe re-deposition is prevented, the area of cathodic sites can be drastically decreased and hence corrosion of Mg can be suppressed. In this proof of concept work we use strong Fe^{3+} complexing agents in order to remove dissolved iron cations from corrosion sites and prevent iron re-deposition. All used iron complexing agents efficiently lowered the corrosion rate of Mg. Direct correlation of complex stability with its inhibiting efficiency was established. It was shown that cyanide, salicylate, oxalate, methylsalicylate and thiocyanate efficiently reduce hydrogen evolution and suppress critical dark area formation.

1. Introduction

It is well known that magnesium is prone to corrosion induced damage not only due to its negative electrochemical potential but also due to its susceptibility to noble impurity elements like Fe, Cu or Ni. Iron, which can be incorporated along the entire processing chain, has especially detrimental impact. Fe-rich particles are the typical sites where corrosion begins since they initiate the microgalvanic corrosion induced anodic dissolution of magnesium [1,2].

Williams et al. [3] showed the occurrence of active persistent cathodic sites on the anodically polarized bare magnesium mainly related to iron-rich particles. Birbilis et al. [4] have shown the enhanced catalytic response of corroding magnesium by measuring enhanced cathodic currents on samples previously held at anodic conditions. It was pointed out that enrichments of noble metals on the exposed surface, with higher exchange current density such as iron, are more favorable sites for the cathodic reaction. Recent publication from Lebouil et al. [5] presented a mechanistic description starting from initial impurity related cathodic reactions towards film formation and its spatial extension. Thomas et al. [6] also stated that the amount of impurities influences the hydrogen evolution rate (HER) which indicates a direct link. Recent studies of Fajardo et al. [7] applying galvanostatic tests proved the impact of impurities even at very low concentrations. Curioni et al. [8] showed that the highest corrosion current is expected close to the corrosion forefront. SVET studies by Williams et al. [9] showing circular expansion of mentioned dark area, also confirm the highest dissolution at the interface to unaffected magnesium and they clearly show that cathodic current contribution over the entire dark film slightly decreases with distance to the interface. The occurrence of transition metal elements like iron on the fully corroded surface was shown by Cain et al. [10]. Very interesting contribution was given by Salleh et al. [11]. Their results state that iron particles entrapped under corrosion products still can sustain HER at high rates. Frankel et al. [12] give a detailed review on the topic. Based on achieved results it can be concluded that dark area suppression is one of the keys to inhibit corrosion of magnesium.

A number of approaches to inhibit corrosion of magnesium have been developed during the last two decades. Eaves et al. [2] showed efficient inhibition by arsenates at acidic conditions. However, with a few exceptions, most of the reported inhibitors aim at suppressing anodic dissolution of Mg. Mesbah et al. [13] used decanoate and heptanoate as anodic inhibitors. Their inhibiting mechanism is based on Mg salt precipitation at the surface (partially protective film). Frignani et al. [14] applied anionic surfactants which apart from adsorbing on the surface also form sparingly soluble salts blocking Mg oxidation. 8-hydroxiqyinoline that forms sparingly soluble complex with Mg was also shown to inhibit Mg dissolution [15–17]. 5,10,15,20-Tetraphenylporphyrin revealed high corrosion inhibition efficiency of 90% by forming chelate complexes with Mg which can precipitate as a film on AZ91D alloy [18]. Nevertheless, the anodic inhibition concept has not reached adequate efficiency level and fundamental mechanistic understanding. For example, 1,2,4-triazole and its derivatives were shown to inhibit corrosion of Mg alloys [19–21] but the inhibiting mechanism has not been explained yet. The environmentally friendly derivatives of lactobionic acid were found to

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* Corresponding author.
E-mail address: Sviatlana.Lamaka@hzg.de (S.V. Lamaka).

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provide 75% to 93% inhibiting efficiency to AZ91 but again, their inhibiting mechanism was not explained while the criteria for selecting said species, were set as being good inhibitors against corrosion of ferrous and not-ferrous metals and having the ability to chemisorb on the metal surface [15].

Latest progress in magnesium corrosion research, based on theoretical work from Flis-Kabulska et al. [22] on iron in alkaline environments, delivers the evidence of chemically active iron at the corrosion forefront. In our recent work Höche et al. [23], we proposed that initial cathodic process on Fe-rich particles and anodic dissolution of Mg around leads to detachment of iron particles from the metallic substrate by undermining or hydrogen bubbles. Self-corrosion of detached Fe-rich particles occurs with formation of Fe^{II} and Fe^{III}. These species can be reduced to metallic Fe chemically (e.g. by adsorbed atomic hydrogen) or electrochemically that leads to deposition of thin metallic Fe film or Fe patches increasing the total cathodic area. Accelerated hydrogen evolution takes place on the freshly deposited Fe due to the increased reactivity of pure metal ("in statu nascendi"). This mechanism points out the straightforward way for corrosion inhibition: if redeposition of dissolved iron is prevented, corrosion rate should decrease. In this work we used several different iron complexing agents to verify whether they indeed influence corrosion rate of magnesium.

2. Material and methods

For the experiments commercial purity magnesium 99.95% (ppm: Fe-220, Ni-2, Cu-5) was used. Impurity content was measured by spark emission spectroscopy. Bare material was cut into pieces, ground, polished and rinsed with ethanol. Hydrogen evolution tests were performed using eudiometers (NS45/27 from Neubert-Glas, Germany). The immersion solution contained 0.5% sodium chloride with or without 0.05 M solution of iron complexing agent. Finally, the samples were observed by optical microscopy. Metrohm-691 pH meter equipped with Mettler-Toledo LabExpert Pt-1000-pH was used for regular pH measurements. OCP was measured using a Gamry Interface 1000 potentiostat in a conventional three-electrode electrochemical cell with a saturated Ag/AgCl reference electrode and a platinum mesh counter electrode. The following chemicals were used Potassium Cyanide, Ref. 1.04967.02 from Merck; Sodium Salicylate, Ref.71945, 5-methylsalicylic acid, Ref.146161 and Sodium Thiocyanate, Ref.251410 all from Sigma-Aldrich and Di-potassiumoxalat monohydrat, Ref.4264.3 from Carl Roth. The pH of all 0.05 M solutions of iron complexing agents was adjusted by NaOH or HCl for the final value varying between 7.5 (for KCN) to 5.9, see Table 1 for more details.

3. Results and discussion

In this communication the first results on the corrosion inhibition efficiency of some iron complexing agents for commercial purity magnesium are presented. Since 1 mol of evolved hydrogen is produced when 1 mol of magnesium dissolves, hydrogen evolution measurements allow direct correlation with inhibiting efficiency. Fig. 1 presents the normalized hydrogen evolution rate (HER) and Fig. 2 visual appearance of the samples immersed in either 0.5% NaCl solution or NaCl solution containing iron complexing agent. The sample exposed to pure NaCl solution shows close to exponential increase of hydrogen evolution, the sample is heavily attacked by corrosion and covered by $Mg(OH)_2$ precipitates. Addition of KCN significantly improves the situation. KCN shows excellent suppression of hydrogen gas formation fully correlated with the surface appearance: three corrosion hotspots occurred while general formation of dark area was strongly suppressed. Note, that even at the very beginning of the immersion test the inhibiting efficiency is rather high, probably coming from both adsorption and iron complexing mechanisms, Fig.1 inset. The OCP values presented in Table 1 vary within similar limits with or without added complexing agents. This indicates that the complexing agents do not change the surface condition to a significant extent.

The weaker complexing agents oxalate and thiocyanate showed intermediate corrosion inhibition performance. The H_2 evolution in their case follows the cyanide's trend but at lower efficiency. It also correlates with the visual appearance of sample surfaces that evidences certain degree of dark area formation and corrosion spots. Interestingly, that HER for oxalate and thiocyanate starts slowly but increases after several hours of immersion. This cannot be explained by lower stability of formed iron complexes at alkaline pH, because pH sharply increases up to 10 and 10.3 during the first hour of immersion (Table 1). More likely, this trend can be explained by the fact that oxalate also forms medium stability complexes with Mg^{2+} which can enhance active dissolution of magnesium, and deplete the complexing agent available for Fe (note that amount of dissolved Fe is roughly 5000 times lower than the amount of dissolved Mg). This explanation, however, is not satisfactory for SCN since it does not form stable complexes with Mg.

Hydrogen evolution trends measured for salicylate and methylsalicylate differ from other discussed complexes. During the first 3 h (for salicylate) and 5 h (for methylsalicylate) no inhibiting effect of salicylates can be seen: hydrogen evolution curves for both complexing agents follow the curve of non-inhibited sample, Fig. 1 inset. Intensive corrosion at the beginning virtually stopped after the first 3 h of immersion in salicylate containing solution. This can probably be explained by the fact that the most stable $Fe^{III}Sal_3$ are formed at higher pH while lower stability complexes $Fe^{III}Sal_2$ and $Fe^{III}Sal$ are formed at neutral pH [24].

The bonding ability of each complex can be described by stability constant K_i. In Table 1 stability constants of Fe^{III} (stable at high pH) and Mg^{II} with the complexing agents are gathered. The cyanide forms highly stable complex with iron while magnesium cyanide immediately hydrolyses and does not exist in solution [25]. Thus, high inhibiting ability of cyanide cannot be ascribed to its interaction with magnesium. Thiocyanate forms much weaker complexes with Fe^{III} that reflects on its corrosion inhibiting performance. In general, direct correlation of inhibiting efficiency with logarithm of stability constant of each iron complexing agent was found, while no direct correlation with stability constant of Mg complex can be seen, Fig. 3. Inhibiting efficiency of thiocyanate, methylsalicylate, oxalate, salicylate and cyanide increases from 69 to 94%. Note, that it was not possible to find stability constants for Mg-cyanide and Mg-methylsalicylate. In Fig. 3, we assumed that the

Table 1
Stability constants of Fe^{III} complexing agents and pH of the solutions used for hydrogen evolution tests shown in Fig. 1.

Complexing agent	*pH of the testing solutions*			*OCP, V vs. Ag/AgCl*		*Stability constants*		
	Before immersion	1 h of immersion	≈24 h of immersion	After 2 s	After 20 min	log $K_{x\,Fe}^{III}$	log K_xMg^{II}	Reference
Cyanide	7.5	n/a	10.5	−1.700	−1.515	K_6 43.9	n/a	[26]
Salicylate	5.9	10.5	11.3	−1.755	−1.709	K_3 36.8	K_1 4.7	[27]
Oxalate	6.0	10.0	11.2	−1.773	−1.625	K_3 20.2	K_2 4.38	[27]
5-Methylsalicylate	6.6	n/a	10.4	n/a	n/a	$K_?$ 9.77	n/a	[28]
Thiocyanate	6.1	10.3	10.8	−1.615	−1.527	K_3 5.0	K_1 −0.9	[29]
NaCl	6.5	10.8	10.9	−1.793	−1.539	–	–	–