Magnesium Technology 2013
Edited by: Norbert Hort, Suveen N. Mathaudhu, Neale R. Neelameggham, and Martyn Alderman
TMS (The Minerals, Metals & Materials Society), 2013

The influence of Mg-Zr master alloy microstructure on the corrosion of Mg

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Keywords: Magnesium, Zirconium, Polarisation, Weight loss, Microstructure

Abstract

In this study, sixteen Mg-Zr alloys were produced to investigate the role of Zr on corrosion of Mg. Alloys were produced using two different commercial Mg-Zr master alloys commonly used for grain refining Mg, but which contain different Zr particle size distributions. It is seen that the master alloy with a smaller Zr particle size leads to an alloy containing more Zr in solid solution. The ratio of Zr in solid solution and in particle form was observed to have a marked effect on the corrosion of Mg.

Introduction

Zirconium (Zr) has a low solid solubility in magnesium (Mg) of 0.73 at.% and it is acknowledged that there are no intermetallic phases that form between Mg and Zr [1]. Zr is commonly and predominantly added to Mg in order to refine the grain size [2-4]. The reduction in grain size in Mg alloys provides greatly improved casting quality and increased mechanical properties [5-7]. As Mg has a Hall-Petch coefficient of 280-320 MPa/μm, the reduction of the grain size in Mg alloys significantly increases the strength of the alloy and allows a greater control over the alloy texture [6, 8, 9]. Thus, Zr is used in the commercial alloys WE43, ZE41 and ZK60. Moreover, newer Mg alloys, such as AM-SC1 and Elektron 21, have recently been developed which also contain Zr for the purpose of grain refinement [10-13]. Given the considerable present interest in Mg alloys a better understanding of the influence of Zr additions on the corrosion of Mg is necessary.

There are reported cases where the addition of Zr to Mg alloys has decreased the corrosion rate through the removal of Fe impurities by the Zr addition [4, 14-16]. Fe impurities in Mg are scavenged by Zr in the melt due to the Zr and Fe combining to form insoluble precipitates, usually Fe_2Zr, which can settle to the bottom of the melt crucible owing to a difference in density. Thus, Mg-Zr alloys are generally considered 'high purity', with commercial Mg alloys that incorporate Zr, usually containing under 50 ppm of Fe [14].

Whilst the removal of Fe by Zr is beneficial in reducing the corrosion rates of Mg alloys, the addition of Zr to the Mg matrix can cause its own corrosion related issues. It has been reported that when Zr is not homogeneously dispersed within the Mg matrix, the corrosion rate can increase compared to a more even distribution of smaller Zr particles [17]. Furthermore, excess Zr in Mg increases the amount of elemental Zr particles that form in the matrix, which is detrimental for corrosion [18]. These elemental Zr particles have been reported to cause micro-galvanic couples with the surrounding Mg matrix and the disruption of the protective oxide film on the alloy surface [19]. As such, further investigation into elucidating the role of Zr in corrosion of Mg is of considerable importance to improve both current and future commercial Mg alloys containing Zr.

In this study, the role of Zr additions on the increasing corrosion rate of Mg and the fundamental effects of different Zr particle sizes and size distributions, added from different Mg-Zr master alloys, is examined. The effect on the corrosion rates for given Mg-Zr alloy mixtures made from two different Mg-Zr master alloys, i.e. Microzir (formally AM-Cast) and Zirmax, are reported.

Experimental Methods

Alloy production and characterization

Sixteen Mg-Zr alloys were produced by adding different amounts of Mg-Zr master alloys to commercially pure Mg. The Mg-Zr master alloys used herein were Microzir, supplied by Magontec, and Zirmax supplied by Magnesium Elektron. Melting was carried out in a resistance furnace using AM-Cover® as a cover gas. The commercially pure Mg was initially melted in a steel crucible at 700°C to which small amounts of the master alloys were added to achieve specific Zr contents in the final castings. The melt was poured into a graphite coated cast iron mould and the ingots were allowed to air cool. Stirred samples were vigorously mixed immediately prior to casting; where as unstirred specimens were held stationary for 20 minutes prior to casting.

The compositions of the alloys were determined independently via inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Spectrometer Services, Coburg, Australia). The precise composition of the experimental alloys is given in Table 1. The values for Zr content in solid solution and overall Zr content were measured by via an acid pre-treatment procedure prior to ICP-AES analysis as per Crawley [20]. The soluble Zr content was determined by dissolving the sample in a 10% HCl solution. The total Zr content was determined by dissolving the specimen in a 50% HCl – 6% HF solution.

Several alloys were examined via scanning electron microscopy. Prepared Mg-Zr alloy specimens and both Mg-Zr master alloys were polished to a 1μm diamond paste finish and then imaged using a JEOL 7001F SEM in back scattered electron (BSE) mode. The microscope was equipped with energy dispersive x-ray spectroscopy (EDX) (Oxford Instruments X-Max 80 detector).

Electrochemical and corrosion testing

Specimen surfaces were ground to a 2000 grit surface finish. A 3-electrode electrochemical flat-cell with an exposed sample area of 1 cm^2 was used in conjunction with a 0.1M NaCl electrolyte. A VMP 3Z potentiostat was used, with potentiodynamic polarisation conducted at 1 mV/s. Prior to polarisation, the samples were conditioned for ten minutes at open circuit to ascertain a stable potential. The polarisation curves were used to determine i_{corr} (via a Tafel-type fit) using EC-Lab software.

Tafel-like fits were executed by selecting a portion of the curve that commenced >50mV from E_{corr}, and i_{corr} was estimated from the value where the fit intercepted the potential value of the true E_{corr}. Polarisation testing was also able to visually reveal comparative information related to the kinetics of both the anodic and cathodic reactions of the various Mg specimens. Each sample was tested five times and an average result was determined.

Additionally, weight loss was determined by exposing alloy samples via immersion in 0.1M NaCl for a period of 24 hours. Subsequent corrosion products were removed by a light scrubbing following a 3s immersion in 15% HNO_3. The mass loss was determined on three unique samples and an average result was determined and reported.

Results and Discussion

Alloy characterization

All alloys examined in this study have Zr additions below the levels expected for grain refinement to take place. Stirring the Mg melt prior to casting was found to increase the overall Zr content in binary Mg-Zr alloys (Table 1). However, while the unstirred alloys had a lower average total Zr content, they did have similar percentages of Zr in solid solution compared to the stirred alloys. The lower total Zr content in the unstirred alloys compared to the stirred alloys is most likely due to Zr particles contained in the unstirred Mg melt settling down to the bottom of the crucible during the extended holding time prior to casting. This would result in less Zr in suspension in the Mg melt at the point in time where the molten liquid is poured from the crucible to the mould while making the Mg-Zr ingot.

The ICP-AES compositional data (Table 1) confirm that the Mg-Zr alloys made from the Microzir master alloy have on average a much higher percentage of Zr in solid solution than the Mg-Zr alloys made from the Zirmax master alloy. The stirred alloys made with the Microzir master alloy averaged between 36% to 47% of the total Zr content in solid solution compared to the stirred alloys made with the Zirmax master alloy which only averaged between 10% to 25% of the total Zr content in solid solution. This difference between the Microzir and Zirmax samples does not appear to be caused by a stirring effect due to the similarities in percentage of Zr in solid solution in both the stirred and unstirred conditions. The difference in microstructure is caused by the different sizes of Zr particles introduced by the Mg-Zr master alloys (Figures 1 (A & B)) [21].

Both the Zirmax and Microzir Mg-Zr alloys (Figures 2 (A, & C)) contain Zr particles embedded in the Mg matrix. EDX mapping elucidates the difference in microstructure of the two alloy groups due to the difference in Zr particles size introduced by the different Mg-Zr master alloys. Apart from the greater number of Zr particles present, there is a large amount of Zr in solid solution in the Mg matrix of the Microzir sample (Figure 2 (B)). The Zirmax alloy (Figure 2 (D)) does not appear to have much Zr in solid solution, despite having a similar overall Zr content to the Microzir alloy. The finer particle sizes introduced by the Microzir master alloy has allowed a greater amount of Zr to go into solid solution rather than forming insoluble Zr particles in the Mg matrix [22]. Due to the very low Fe content in both of the Mg-Zr alloys, no discernable Fe peaks of note were seen while performing EDX testing on the selected specimens.

There is a noticeable difference in the Zr particle structure between the two Mg-Zr alloy groups. The Microzir alloys generally have smaller Zr particles that cluster together, compared to the Zirmax alloys that have larger and more isolated individual Zr particles. Again, the difference in particle size between the two master alloys is likely to be the cause for the different morphologies in the Zr particles present in the matrix. Vigorous stirring has been shown to minimise the presence of large Zr particle clusters, however, larger individual Zr particles need longer holding times to let the particles settle out of the Mg melt effectively [23]. The extended holding times required to remove the larger individual Zr particles have been shown to reduce the overall Zr content in the Mg alloy. The EDX map of the selected Microzir and Zirmax specimens corroborates the compositional analysis which indicate that the Microzir alloys have a much higher percentage of Zr in solid solution compared to the Zirmax alloys.

Assessment of Zr in solid solution

There is a higher average Zr content in the stirred Mg-Zr alloys compared to the unstirred alloys (Figure 3 (A & B)). This is due to the fact that more Zr particles are able to settle to the bottom of the crucible during processing of the unstirred samples, which were held motionless for an extended period of time prior to casting. It can be seen that there is a trend where the overall percentage of Zr in solid solution increases as the overall Zr content increases in the Microzir containing alloys (Figure 3 (A)). The Zirmax alloys, however, show the opposite effect, in that as the overall Zr content increases the percentage of Zr in solid solution decreases. Despite the reduced uptake of Zr in Mg overall, these trends are also seen in the unstirred Mg-Zr alloys (Figure 3 (B)).

The amount of Zr in solid solution is influenced by the difference in Zr particle size characteristic of the two master alloys. The Zirmax master alloy has a larger and more variable Zr particle size compared to the Microzir master alloy, which has a more even distribution of smaller Zr particles [22, 23]. The finer Zr particle size in the Microzir master alloy, with most Zr particles ranging between 1 and 5 μm in size, allows for more Zr to dissolve into solid solution. This finer distribution is highly desired due to the beneficial effects favouring the alloying effectiveness of the Mg-Zr master alloy and the ensuing grain-refining effect of Zr [4, 24-26]. Moreover, with more Zr in solid solution, less elemental Zr particles will be retained in the Mg matrix to contribute to corrosion related problems and increased corrosion rates.

Effect of Zr alloying additions on Mg corrosion rates

I_{corr} increases in the Zirmax containing alloys as the Zr content in solid solution increases (Figure 4 (A)). The Zirmax alloys, however, typically have only low levels of Zr in solid solution with increasing total Zr content, with only up to 0.012 wt.% Zr observed in solid solution at best. The Microzir alloy, with over 0.1 wt.% Zr in solid solution, displays an initial slight decrease in i_{corr} before increasing, however, the later increase does not exceed the initial measured i_{corr} value.

The i_{corr} values for the Zirmax alloys appear to be quite variable with very little increase in Zr content in solid solution (Figure 4 (B)). The Microzir alloys, with a slightly higher percentage of Zr in solid solution, do have some semblance of a decreasing corrosion rate. There is initially a drop in the measured i_{corr} value as the Zr content in solid solution is increased. However, the overall Zr content is still quite low (Table 1).

In the Microzir alloys, i_{corr} decreases, then increases slightly as the overall Zr content increases (Figure 4 (C)). The higher percentage of Zr in solid solution allows for higher overall Zr contents in Mg before accelerating the corrosion rate. The Microzir-4 alloy contains five times as much Zr in solid solution as the Zirmax-4 alloy with a similar total Zr content. The greater amount of Zr present as elemental Zr particles in the Zirmax alloys thus contributes to increased i_{corr} values than the Microzir produced Mg-Zr alloys.

The stirred and unstirred samples do not have a similar measured i_{corr} trend. There is an overall decrease in i_{corr} for the unstirred Microzir alloys and a slight overall increase for the unstirred Zirmax alloys (Figure 4 (D)) compared to stirred alloys of a similar content. The greater percentage of Zr in solid solution at a lower overall Zr content in the unstirred Microzir alloys compared to the stirred alloys may account for this difference as a greater amount of Zr has gone into solid solution. The unstirred Zirmax alloys have a lower percentage of Zr in solid solution compared to the stirred alloys with a similar Zr content. The greater amount of Zr particles embedded in the matrix, rather than dissolving into solid solution, is the likely cause of the increase i_{corr} values measured.

Influence of Zr on the corrosion reaction kinetics of Mg

As Zr is introduced into Mg there is an increase in the anodic reaction kinetics whilst the cathodic reaction kinetics are only slightly increased for the Zirmax containing alloy. The changes in the reaction kinetics when Zr is added can be seen in Figure 5. The increase in anodic and cathodic reaction kinetics can be observed through the shifts in the anodic and cathodic branches of the polarisation curves compared to pure Mg. At the alloying content limit of the Mg alloys examined (Table 1), Zr is still below the solid solution limit in Mg according to the phase diagram [1], with a large percentage of the total Zr content in the Mg-Zr alloys in solid solution.

The data reveals that Zr is an anodic activator of Mg and increases the corrosion rate of Mg when added. This anodic activation effect is observed even at very low levels of Zr and does not seen to be influenced by the initial microstructure of the Mg-Zr master alloy used in the manufacturing of the Mg-Zr alloys. This data supports previous work that the initial addition of Zr into Mg increases the anodic kinetics before increasing the cathodic reaction kinetics via micro-galvanic coupling with large Zr particles embedded in the Mg matrix [27]. The increase in anodic kinetics is the key electrochemical reason for the increased corrosion rates seen in the Mg-Zr alloys produced herein. As such, the increase in the cathodic reaction kinetics in the Zirmax containing Mg-Zr alloy can be explained by the increased number of large Zr particles present in the microstructure due to less Zr dissolving into solid solution.

Comparison between Microzir and Zirmax alloys via long corrosion testing

There is a noticeable trend linking the overall Zr content and the mass loss from immersion results (Figure 6). The relationship shows that as the Zr content increases the mass loss also increases per unit time. The data is presented in its native units to avoid problems or errors from assuming uniform corrosion for the immersion weight loss data data.

There is a divergence in the weight loss values for the two Mg-Zr alloy groups. The Microzir alloys not only have a higher average weight loss than the Zirmax alloys but they also have a larger calculated standard error. As the two alloy groups have a similar overall Zr content (Table 1), the most likely cause for the increased weight loss observed in the Microzir alloys is the higher Zr content in solid solution.

General discussion

The increase in Zr content in Mg has a great influence on the anodic corrosion characteristics of Mg. As discussed previously, however, there is no large overall increase in i_{corr} with increasing Zr content in the Microzir alloys, Figure 6 shows that when there is a greater amount of Zr in solid solution there is an increase in the corrosion rate according to the longer term immersion weight loss tests.

The higher levels of Zr in solid solution lead to a greater anodic activating effect in the Mg matrix. This is an indicator that there is a greater anodic activation by the higher amount of Zr in solid solution increasing the long-term corrosion rates. With a higher Zr content in solid solution there should be a greater amount of generalised corrosion attack across the surface area of the alloy as less Zr particles would be present in the matrix to serve as corrosion initiation sites via micro-galvanic coupling.

Despite the desire for a greater content of Zr in solid solution, which is beneficial for grain refinement [27], even low levels of Zr appear to increase the overall corrosion of Mg. The difference in the size of the Zr particles introduced to Mg does appear affect the way in which Zr affects the long-term corrosion rate. Higher percentages of Zr in solid solution for a given total Zr content increase the long-term corrosion rates of Mg, where as lower percentages of Zr in solid solution for a similar Zr content will have a greater impact on the short-term electrochemical corrosion behaviour of Mg.

While other studies have suggested that the addition of Zr is favourable for corrosion resistance of Mg [14, 15], these studies have generally examined Mg-alloys that contain other elements, such as rare earths. As such, they do not reflect the direct interaction between only Zr and Mg. Any decrease in corrosion rates observed in such studies are likely from secondary interactions between Zr and ternary or quaternary elements or the changes in grain sizes - which in turn also impact the corrosion of the particular alloys studied.

Conclusions

1. For the same nominal composition, higher overall Zr contents were obtained through stirring of the Mg melt prior to casting due to settling of Zr in the furnace crucible with the long holding times associate with the unstirred alloys.
2. Stirring of the melt did not greatly affect the average percentage of Zr in solid solution for a given total Zr content.
3. Mg-Zr master alloys with a finer particle size used in the production of Mg-alloys will have an increased amount of Zr in solid solution in Mg-alloys for a given Zr content.
4. The corrosion current density, i_{corr}, increases more significantly with an increasing Zr content when there is a lower percentage of Zr in solid solution.
5. Zr in solid solution in Mg is an anodic activator, increasing the anodic reaction kinetics and thereby accelerating the generalised corrosion attack of the matrix.

6. Mass loss testing indicated that greater (and more highly variable) mass loss occurs with time in alloys which have a higher proportion of Zr in solid solution.

Acknowledgments

The CAST Co-operative Research Centre was established under, and is funded in part by, the Australian Governments Co-operative Research Centres Scheme. Andy Yob, Ming Sun and Sherly Simanjuntak are gratefully acknowledged for their assistance in preparing the alloys used in this research.

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Figure 1: (A): BSE-SEM micrograph of Microzir master alloy, (B): BSE-SEM micrograph of Zirmax master alloy. **Figure 2**: (A): BSE-SEM micrograph of Mg-0.22Zr Microzir alloy, (B): EDX map of Zr content in Mg-0.22Zr Microzir alloy, (C): BSE-SEM micrograph of Mg-0.19Zr Zirmax alloy, (D): EDX map of Zr content in Mg-0.19Zr Zirmax alloy.

Figure 3: (A): Zr in solid solution vs. total Zr content for stirred Mg-Zr alloys (B): Zr in solid solution vs. total Zr content for unstirred Mg-Zr alloys.

Figure 4: (A): Zr content in solid solution (wt.%) vs. i_{corr} for stirred Mg-Zr alloys, (B): Zr content in solid solution (wt.%) vs. i_{corr} for unstirred Mg-Zr alloys, (C): Total Zr content (wt.%) vs. i_{corr} for stirred Mg-Zr alloys, (D): Total Zr content (wt.%) vs. i_{corr} for unstirred Mg-Zr alloys.

Figure 5: Electrochemical polarisation curves for Microzir and Zirmax containing Mg-Zr alloys compared with commercially pure Mg.

Figure 6: Weight loss vs. Zr content for Mg-Zr alloys made with Microzir and Zirmax master alloys.

Sample ID	Mg wt.%	Zr wt.% (Total content)	Overall % of Zr in solid solution	Fe wt.%
Microzir-1 Stirred	~Bal	0.028	42.86	0.01
Microzir-1 Unstirred	~Bal	0.012	33.33	0.008
Microzir-2 Stirred	~Bal	0.061	36.07	0.01
Microzir-2 Unstirred	~Bal	0.014	42.86	0.008
Microzir-3 Stirred	~Bal	0.12	45	0.011
Microzir-3 Unstirred	~Bal	0.019	47.37	0.005
Microzir-4 Stirred	~Bal	0.22	47.27	0.014
Microzir-4 Unstirred	~Bal	0.037	51.35	0.006
Zirmax-1 Stirred	~Bal	0.028	25	0.006
Zirmax-1 Unstirred	~Bal	0.018	22.22	0.006
Zirmax-2 Stirred	~Bal	0.057	15.79	0.006
Zirmax-2 Unstirred	~Bal	0.025	16	0.005
Zirmax-3 Stirred	~Bal	0.12	10	0.001
Zirmax-3 Unstirred	~Bal	0.056	8.93	0.005
Zirmax-4 Stirred	~Bal	0.19	10.53	0.006
Zirmax-4 Unstirred	~Bal	0.075	8	0.013

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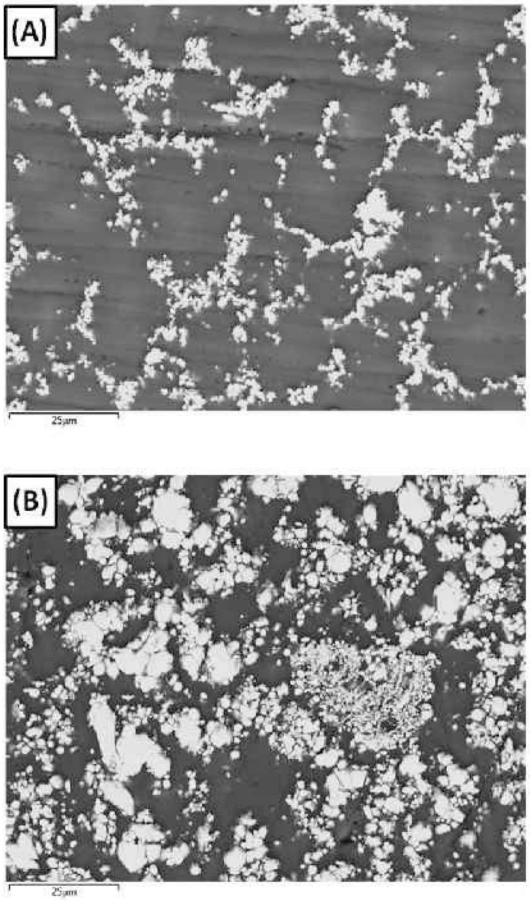

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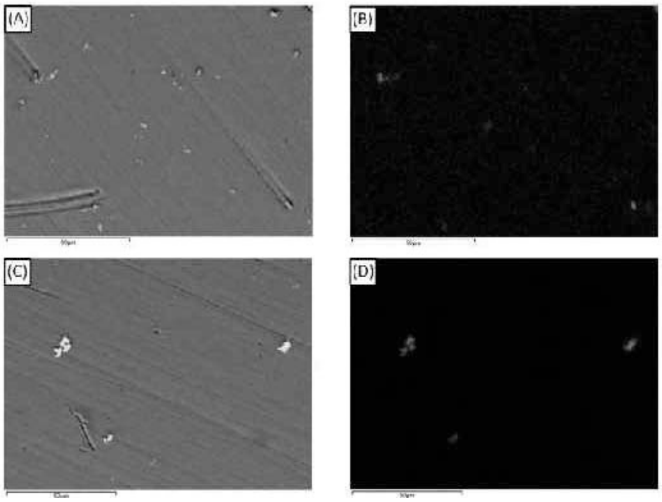

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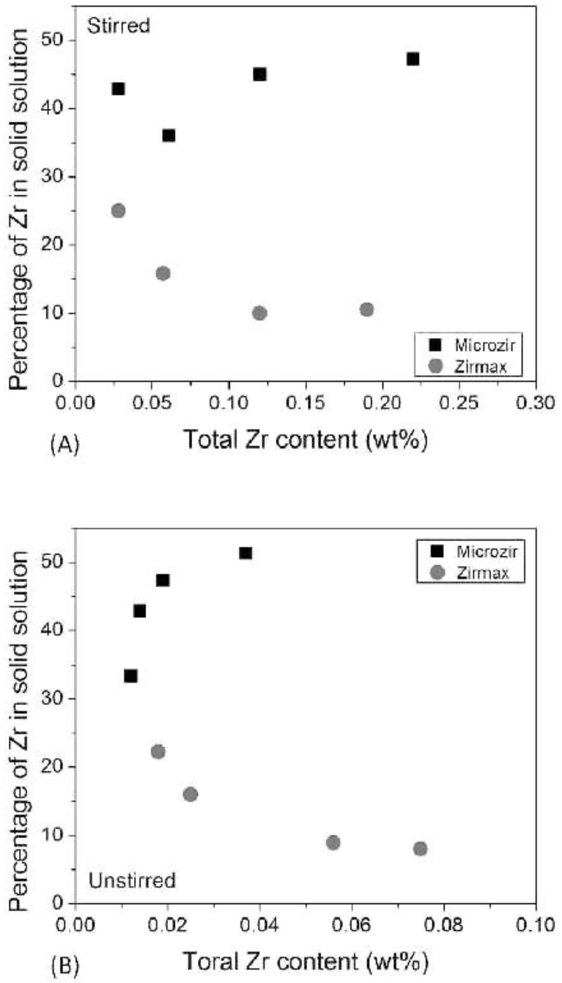

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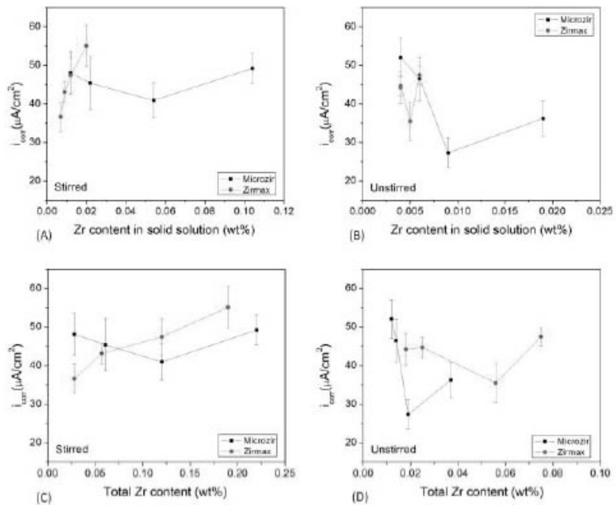

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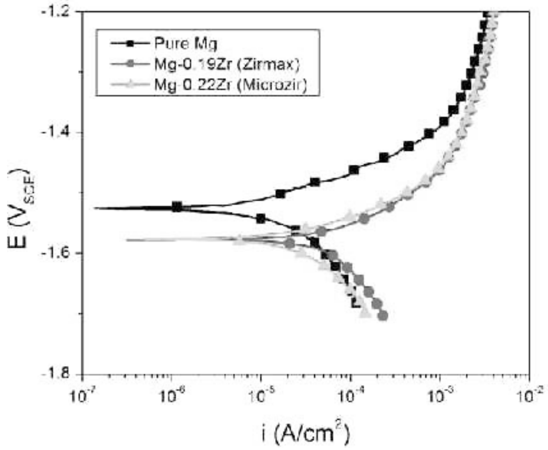

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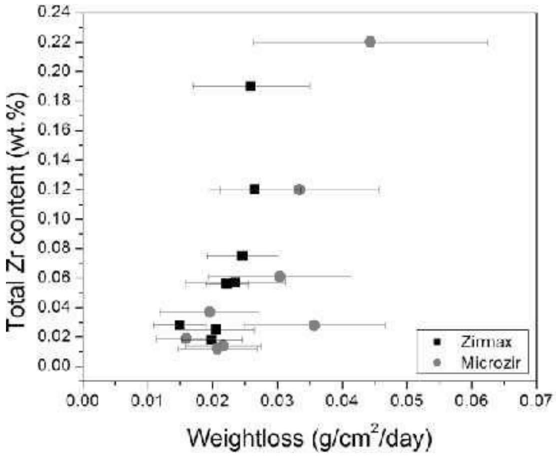

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