Effect of manganese addition on anode characteristics of electrolytic magnesium

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Abstract

Purpose – The purpose of this paper is to investigate the influence of manganese addition on sacrificial anode characteristics of electrolytic magnesium.

Design/methodology/approach – Different contents of manganese were added to magnesium. Anode characteristics were evaluated and correlated to added manganese.

Findings – The performance of an anode depends strongly on the manganese content. An optimum value for the manganese to be added was identified. The impurity levels to obtain efficiencies above 50 per cent also are reported.

Originality/value – This paper highlights the properties of magnesium-manganese binary alloys for use as sacrificial anodes in cathodic protection.

Keywords Alloys, Corrosion protection, Cathodic protection

Paper type Research paper

Introduction

The use of magnesium alloys for cathodically protecting steel structures is well established (George *et al.*, 1956; Heideman and Halford, 1962; Fisher, 1964; Bernard, 1968; Vrable, 1971; Woody, 1976; Fitzgerald and Kolb, 1985). They are used to protect storage tanks, buried structures, pipelines, etc. where the resistivity of the environment is relatively high (as high as 6,000 ohm.cm). These alloys primarily contain aluminium, zinc, zirconium, calcium, etc. as alloying elements (Robinson, 1946; Humble, 1948; Osborn and Robinson, 1952; Subramanyan *et al.*, 1980; Balakrishnan *et al.*, 1987; ASTM, 1993; DIN, 1998). Several patents exist internationally for the above alloys (Indian Patent Number 146925; Indian Patent Number 168411; German Patent Number 542054; British Patent Number 411324).

Among the above-mentioned alloying elements, manganese is reported to be the major element that contributes to the improved anode characteristics of these alloys. This is achieved by enveloping or settling along with or forming intermetallic compounds with the impurities (Nelson, 1944; Robinson and George, 1954; Zamin, 1981). The above-three processes mitigate the detrimental effect of the impurities, especially that of Iron. Studies conducted on the effect of minor level of impurities on corrosion of magnesium (Hanawalt *et al.*, 1942; Roberts, 1960), recommended the following limits: iron 170 ppm, copper 130 ppm and nickel 50 ppm.

Beyond these limits, the corrosion rate of magnesium increased rapidly. In the present work, the performance of magnesium alloys containing different quantities of manganese, prepared using electrolytic magnesium is presented.

Methodology

A series of magnesium alloys with different manganese contents were cast using electrolytic magnesium and different quantities of 99.95 per cent manganese. Samples of 1 cm diameter and 7 cm length were prepared from each alloy for experimentation. Samples were cleaned in boiling chromic acid with silver chromate solution, before and after experiments. The following experiments were carried out: chemical analysis, open-circuit potential (OCP) measurements, closed-circuit potential (CCP) measurements, self-corrosion tests, anode efficiency tests and metallography. The surface condition of samples was examined after the efficiency tests. Analytical reagent grade chemicals and distilled water were used to make up the environment/media. The environment used to characterize anode performance was saturated calcium sulphate + magnesium hydroxide, which corresponded to a relatively high-resistivity environment. A standard calomel electrode (SCE) was used as the reference electrode.

Chemical analysis

The chemical analysis was carried out using a Hilger Attest S spectrophotometer. Each alloy was analyzed in triplicate for Mn, Fe, Al, Zn, Cu and Ni and the results for each element were averaged to obtain the chemical composition.

Open circuit potential test

Three samples of each alloy, 1 cm diameter and 7 cm length, with provisions for electrical contact, were immersed

in different cells containing the specified medium. On immersion, the potential of the sample was measured, with respect to SCE, after 1 h for the first 4 h and then after every 24 h, until 96 h. Then the values were averaged for each sample to get the OCP of the alloy.

Closed circuit potential test

Alloy samples (in triplicate) of size 1 cm diameter and 7 cm long, were immersed in the specified medium and connected to the positive end of a power source. Cylindrical stainless steel electrodes surrounding each alloy sample were connected to the negative terminal. A current equivalent to $1\,mA/cm^2$ was applied. The potential of the anode was measured against SCE after every 1 h for the first 4 h and then after every 24 h, for a total of 96 h. The potentials were averaged for each alloy to evaluate the value recorded as the CCP.

Self-corrosion test

Samples in triplicate, 1 cm diameter and 7 cm long, were cleaned, dried and weighed. They were lacquered, leaving exposed only about $16.5\,cm^2$ of the surface area. The samples then were immersed in the specified medium for a period of 96 h. After the above period, the samples were removed from the environment, cleaned, dried and weighed. From the weight loss, the corrosion rate of each sample was calculated and averaged for each alloy.

Anode efficiency test

Tests were carried out with specimens of 1 cm diameter and 7 cm length with an actual exposure area of $16.5\,cm^2$ after suitable masking, in the specified medium, in accordance with ASTM G 97-97 (2002). The efficiency tests were carried out at different current densities, from 10^{-5} to $10^{-3}\,A/cm^2$, using stainless steel as the cathode. The resulting weight loss at each current density was used to calculate the efficiency of the anode. The average efficiency for each alloy was calculated at each current density.

Metallography

A cross section of a specimen from pure magnesium and the alloy with the optimum anode performance was polished for metallography using 1/0, 2/0 and 3/0 emery papers. Then the surface was polished to a mirror finish using a polishing wheel. The polished surface was etched using 2 per cent oxalic acid solution to reveal the microstructure for analysis.

Corrosion morphology

The surface condition of each sample after every individual test was visually observed and recorded. In addition, cross-sections of tested samples were scanned using an optical microscope, to identify the presence of inter-granular attack (if any).

Results

Chemical analysis

The compositions of the alloys studied are listed in Table I and have been compared with that of pure magnesium. The manganese content had been varied in the range 0.06-0.65 per cent (by weight). The impurity content, especially that of Fe, was controlled to be within 0.006 ± 0.002 per cent.

Table I Chemical composition of magnesium alloys

Metal	Manganese (per cent)	Iron (per cent)	Others (per cent)	Magnesium (per cent)
A (pure Mg)	0.0000	0.2700	<0.005	Balance
B	0.0661	0.0086	<0.005	Balance
C	0.1398	0.0069	<0.005	Balance
D	0.1841	0.0053	<0.005	Balance
E	0.4031	0.0055	<0.005	Balance
F	0.5638	0.0057	<0.005	Balance
G	0.6268	0.0054	<0.005	Balance

Other elements such as Cu, Ni, Si, Al and Zn were present at <0.005 per cent.

Open circuit potential

It was observed that with the addition of manganese, the OCP shifted in the more negative direction, initially, up to a manganese content of about 0.18 per cent, beyond which it shifted towards the less-negative direction, within the composition range studied, as given in Table II. However, the variation was observed to be relatively less, i.e. the OCP values lay within $\pm 25\,mV$.

Polarization

It was observed that these alloys polarized by about 0.200-0.300 V, cathodically, on application of high current, but yet sustained considerable driving potential (0.250-0.450 V), for a protective potential of $-0.850\,V$ (wrt SCE) for buried steel structures. In addition, the highest driving potential was attained by the alloy with about 0.18 per cent manganese, after which the driving potential fell slightly with increase in manganese content. The effect of polarization on these alloys is shown in Figure 1.
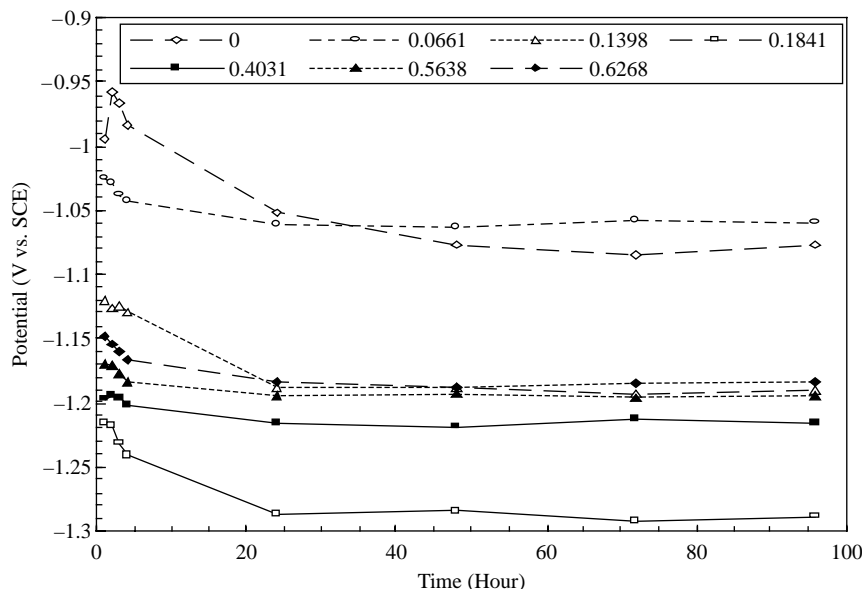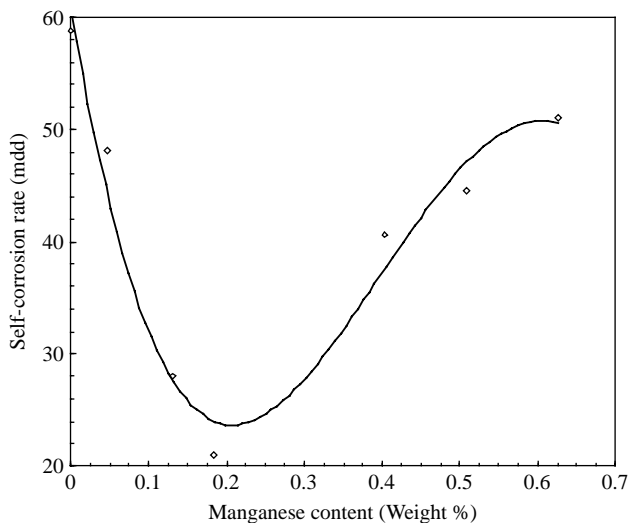
Self-corrosion

The variation in corrosion rates of the Mg alloys with manganese content is shown in Figure 2. It was observed that as the manganese content was increased up to 0.18 per cent manganese, the corrosion rate of the alloys decreased. Beyond 0.18 per cent manganese, the corrosion rate was observed to increase relatively gradually.

Anode efficiency

The anode efficiencies at different current densities for each alloy were observed to increase with increase in current

Table II OCP of the magnesium alloys

Time (h)			Open-circuit potential (V vs SCE)				
	A	B	C	D	E	F	G
1	−1.335	−1.373	−1.351	−1.373	−1.375	−1.365	−1.353
2	−1.341	−1.375	−1.357	−1.375	−1.373	−1.368	−1.359
3	−1.344	−1.385	−1.356	−1.389	−1.374	−1.373	−1.365
4	−1.345	−1.390	−1.361	−1.398	−1.380	−1.379	−1.372
24	−1.437	−1.408	−1.402	−1.445	−1.394	−1.391	−1.389
48	−1.434	−1.41	−1.419	−1.441	−1.397	−1.389	−1.393
72	−1.443	−1.405	−1.424	−1.449	−1.391	−1.399	−1.39
96	−1.441	−1.406	−1.421	−1.446	−1.394	−1.391	−1.389
Average	−1.441	−1.406	−1.421	−1.446	−1.394	−1.391	−1.389

Figure 1 Effect of manganese content on CCP

Figure 2 Effect of manganese content on self-corrosion rate

density for all the alloys studied. This was due to the fact that self-corrosion or "parasitic corrosion" was suppressed by the applied current density. Also at practical current densities of around $0.5\,mA/cm^2$, the alloy with about 0.18 per cent manganese exhibited an anode efficiency > 50 per cent. Here, the efficiency curves shifted away from the X-axis as the manganese content was increased to 0.18 per cent and as the manganese content was increased further, the curves gradually fell towards X-axis, as shown in Figure 3. This also reinforced the fact that about 0.18 per cent manganese was the optimum content among the alloys studied.

Metallography

The microstructures of pure Mg and the 0.18 per cent manganese alloy were analyzed to gain a better understanding their behaviour. Pure Mg, in the as cast condition, had large grains, i.e. a coarse structure. With the addition of manganese, the structure was modified considerably. It changed from a simple coarse-grained structure (that of pure Mg), to a fine grained structure As the manganese content was increased, the structure was observed to be refined up to about 0.18 per cent. The microstructures exhibited relatively a fine structure as manganese content increased further, but in addition to the refined grains, the presence of inter-metallic particles and precipitates also were observed. This is in accordance with that the findings reported (Beck, 1943).

Corrosion morphology

A marked influence on the corrosion pattern of Mg was observed with the addition of manganese. Pure Mg exhibited severe pitting with ridges and craters after the self-corrosion tests and efficiency tests at current densities $> 200\,\mu A/cm^2$. At lower current densities, only pitting occurred. On adding manganese, the surface morphology changed along with manganese content. The alloy with 0.06 per cent manganese exhibited no ridges but shallow pits having larger diameter in many areas, while the remaining area exhibited almost uniform attack, after testing at all current densities. The uniformity in attack increased with increase in manganese content up to 0.18 per cent. The alloy containing 0.18 per cent Manganese exhibited almost uniform attack. Pitting was considerable in alloys with higher manganese contents.

Discussion

The variation in OCP values for each alloy lay in a narrow range. The CCP values for each alloy varied over a small range and were in the acceptable level for alloy with optimum manganese content only. The maximum reduction in self-corrosion rate and the associated improvement in anode efficiency for the optimum manganese addition indicated that the detrimental effect of iron was overcome significantly.

The variation in self-corrosion rate could be attributed to the nature and stability of the $Mg(OH)_2$ film formed on

Figure 3 Effect of manganese content on anode efficiency at different current densities
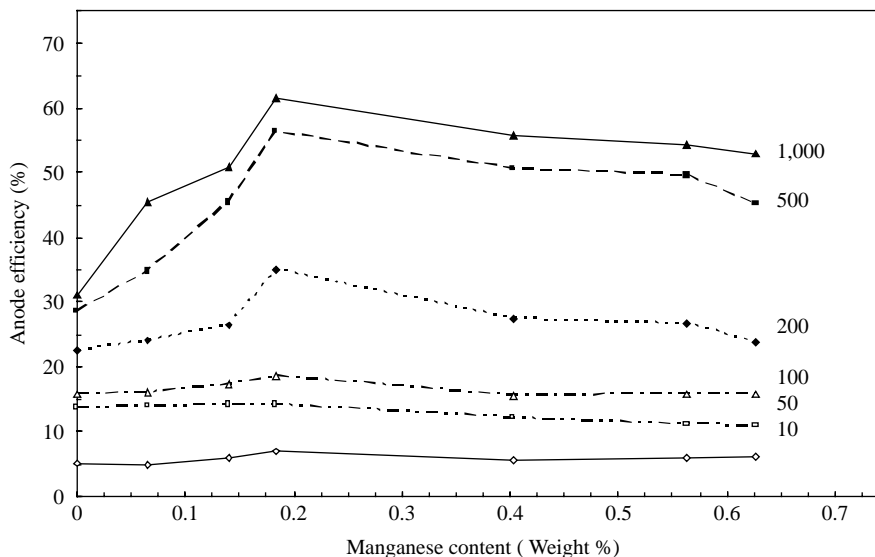
exposure to the environment. This film, as a natural consequence of its good electrical insulating properties, acts as an effective physical barrier (Emley, 1966). The film was able to render maximum protection when manganese content was about 0.18 per cent. Beyond that concentration, the film was weakened and its protective nature decreased due to increase in number of inclusions on the surface, which weaken the adherence of the surface film to the substrate.

This presence of the inter-metallic particles (as inclusions) could be the cause of the deterioration in anode characteristics of Mg alloys containing manganese >0.18 per cent. The local cell action and its deleterious effect on the $Mg(OH)_2$ film formed decrease the anode efficiency. The presence of more inclusions in the microstructure beyond 0.18 per cent manganese also substantiates the above.

The distribution of the alloyed manganese and the lower impurity content in the matrix also controls anode characteristics. Lower manganese content will be unable to suppress the effect of impurities (especially that of iron). Higher manganese contents lead to the formation of precipitates, which in turn increase the local galvanic cells and enhance anode consumption.

Conclusions

Alloying manganese with magnesium and controlling the iron content to about 0.006 per cent and <0.005 per cent for other impurities significantly improves the anode characteristics of the alloy.

The improved anode characteristics were attributed to the optimum distribution of the manganese in the solid solution and precipitates or inter-metallics.

The alloy containing 0.18 per cent manganese exhibited superior anode characteristics such as lowest self-corrosion rate and highest anode efficiency (at practical current densities) of the alloys studied, and is suitable for use as a sacrificial anode wherever Mg alloys of similar capacity are used.

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