Effect of Heat Treatment on the Corrosion Resistance of Modified Aluminum-Magnesium Alloys in Seawater

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Study of modified Al-2.5Mg alloys containing chromium, silica, iron, and manganese in various tempers (O, H-18, T-4, T-6, T-18, and H-34) has shown that their corrosion resistance is significantly altered by thermomechanical treatment and the beneficial effect of chromium on microstructural changes. Modified binary Al-2.5Mg alloys in the T-6 and T-4 tempers exhibit a higher resistance to corrosion in Arabian Gulf water than H-34 tempers due to the beneficial effect of chromium on microstructural changes.

1. Introduction

ALUMINUM alloys containing magnesium, manganese, silicon, and chromium have demonstrated promising application potential in multi-stage flash (MSF)-type desalination plants by virtue of their good resistance to corrosion in hot seawater.[1,2] Generally, aluminum alloys are next to titanium and copper alloys when used for heat transfer tubes in MSF-type desalination plants.[3] Wider use of aluminum alloys has, however, been restricted by problems on the design and maintenance sides and the tendency of these alloys to pitting under long-term use.[4] There are many examples of successful application of these alloys in hot seawater in many countries.[5]

Metallurgical treatment of aluminum alloys is necessary to obtain desired mechanical properties. Variations in thermal treatments are known to affect the corrosion resistance of aluminum alloys because of the change brought about in microstructure.[6,7] The composition, quantity, and distribution of phases and their corrosion potential relative to the solid solution matrix is reported to have an important bearing on corrosion resistance.[8]

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Attempts have been made in recent years to improve the corrosion resistance of aluminum-magnesium binary alloys in seawater by alloy modification.[9] The corrosion resistance of such alloys in various tempers has been reported in literature; however, the data on the effect of heat treatment on the corrosion resistance of these alloys in seawater are limited.

A study was therefore undertaken to evaluate the corrosion resistance of two modified Al-2.5Mg alloys in the O, H-18, H-34, T-1, and T-6 tempers in Arabian Gulf water. The results of the investigation are described below.

2. Experimental Procedure

2.1 Materials

Compositions of the experimental alloys are given in Table 1. All tests were conducted in deaerated Arabian Gulf water at 25 ± 1 °C. The composition of the Arabian Gulf water is given in Table 2. Alloy 1 and 2 in the O, H-18, H-34, T-4, and T-6 tempers were investigated. Details of temper designations are

O: Annealed at 350 °C for 3 h

H-18: Strained hardened by rolling

H-34: After intermediate annealing (350 °C/30 min), at 4.4-mm thickness rolling to 2.0 mm, stabilized for 3 h

T-4: Solution treated (525 °C/30 min), water quenched, and naturally aged

T-6: Solution treated (525 °C/30 min), water quenched, and artificially aged for 12 h

Table 1 Composition of the modified aluminum alloy

Alloy No.	Composition, wt%								
	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Al
1	0.67	0.10	<0.01	<0.01	2.66	<0.01	0.02	0.003	Bal
2	1.01	0.16	<0.01	<0.1	2.48	0.22	0.01	0.003	Bal

Table 2 Analysis of Arabian Gulf water

Ions	Analysis, mg/L							
	Na^-	Ca^{--}	Mg^{--}	SO_4^-	Cl^-	CO_3^-	HCO_3^-	Total
Arabian Gulf Water	19,186	704	2400	4894	34,080	18	189	61,471

Fig. 1 Mg$_2$Si precipitates in alloy 1.
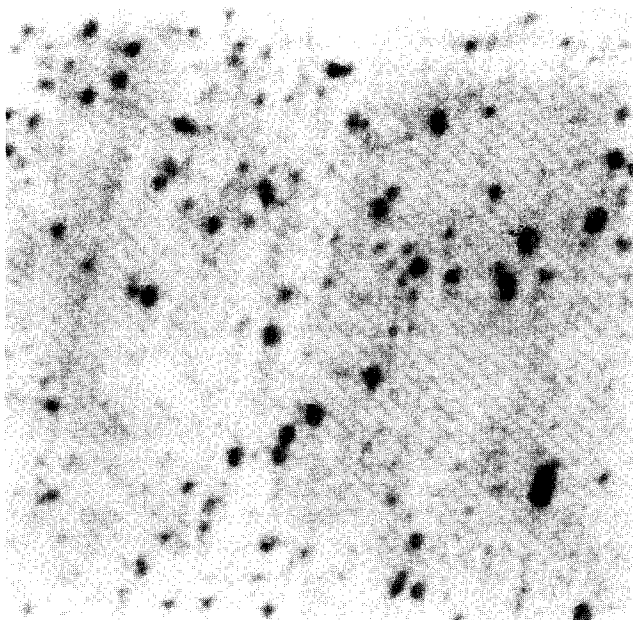

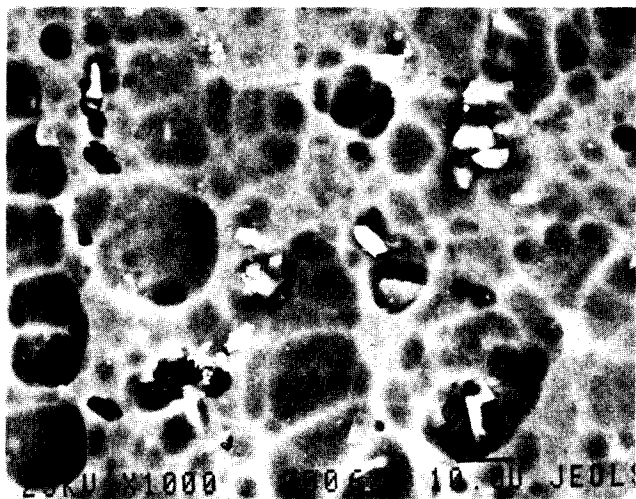**Fig. 3** Typical polarization plot for alloy 1 in the T-4 condition.

Fig. 2 Second-phase particles containing silica, iron, and chromium in alloy 1.

2.2 Specimen Preparation

For metallographic studies, the samples were cut to 1.5-cm diameter and mounted in bakelite. Grinding was done with 600-grit silicon carbide paper, and final polishing with 0.5-μm aluminum paste in distilled water. For scanning electron microscopy (SEM) examination, the samples were ultrasonically cleaned with acetone and dried with hot air. They were gold coated to a thickness of 0.2 nm (2 Å) at 1200 V under a vacuum of 10^{-3} torr for 5 min. For corrosion testing, specimens in the form of discs with a diameter of 1.5 cm were used. All samples were treat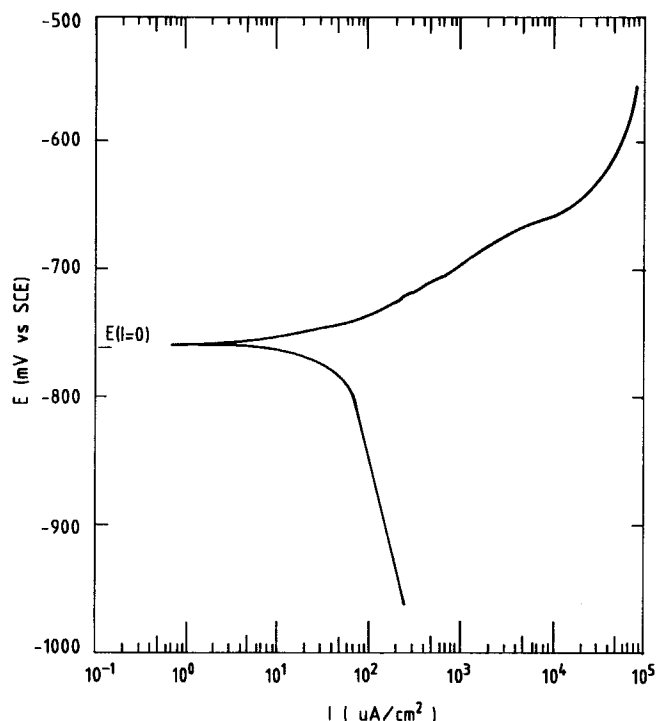ed with a hot commercial detergent solution and then rinsed with potable water. The samples were later exposed for 5 min in boiling petroleum benzene and ethanol at 380 °C and 5% acetic acid at 48 °C. Specimens were finally rinsed with demineralized water, degreased with acetone, and dried for 24 h.

2.3 Polarization Measurements

Potentiodynamic polarization techniques in accordance with ASTM standard G61-86 were used to evaluate the corrosion resistance of the alloys. A microprocessor-based EG & G model 273 Potentiostat-Galvanostat* was used for polarization measurements. The above instrument was programmed to obtain Tafel, linear polarization, and potentiodynamic polarization plots after allowing the potential to be stabilized for at least 6 h prior to the beginning of the experiment.

3. Results and Discussion

Magnesium is the primary alloying element that controls the basic characteristics of the structures in binary aluminum-magnesium alloys. None of the other elements affect the structure substantially, because they are not added in amounts that are sufficient to radically change the equilibrium. The aluminum-magnesium diagram is well established. In the experimental alloys 1 and 2, the magnesium content is less than 3%; hence, most of the magnesium is present in the solid solution. However, Mg$_2$Al$_3$ may be formed under nonequilibrium conditions.[10,11]The amount of silicon in experimental alloy 1 and

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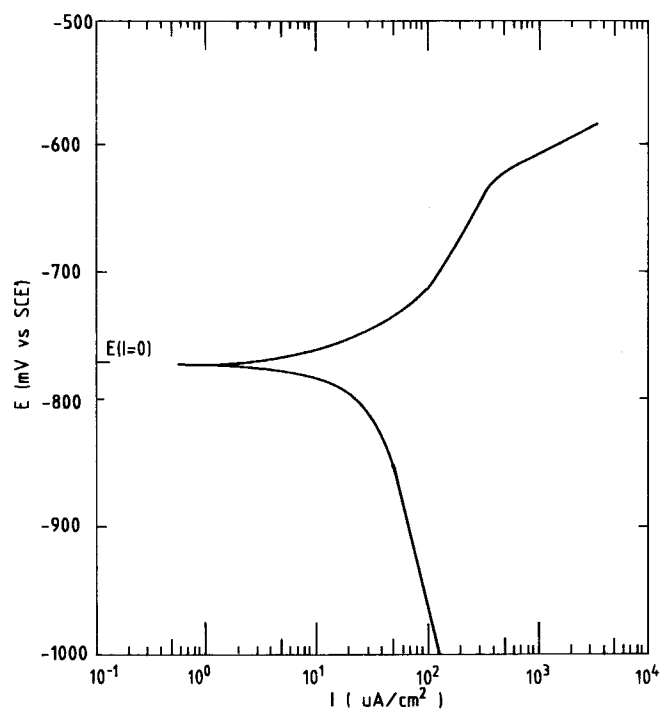* Product of EG&G, Princeton Applied Research, Princeton, NJ 08450.

Fig. 4 Typical polarization plot for alloy 2 in the H-34 condition.

Fig. 5 Dissolution of grain boundaries and some intergranular attack on alloy 1 in the H-18 temper.

Fig. 6 Slight attack on grains in a preferred orientation in alloy 1 in the T-4 temper.

Fig. 7 Network of precipitates in alloy 2 (H-34 temper).

2 ranges from 0.67 to 1%. It is present primarily as Mg_2Si precipitate in alloys 1 and 2. Figure 1 shows the Mg_2Si precipitate in alloy 1. Manganese is present in these alloys as an impurity element, and it remains in solid solution. Alloy 2 contains chromium (0.22%), whereas the chromium content in alloy 1 is only trace amounts. Most of the iron is present in alloys 1 and 2 as intermetallic second phase (ΦAl_3Fe) in combination with aluminum, silicon, and chromium.

By calorimetric and microstructural studies (EPMA, TEM), the existence of Mg_2Si and (ΦAl_3Fe) has been confirmed.[12] Upon homogenization, C-Al Fe (Mn, Cr, Si) particles develop

from (ΦAl_3Fe) by incorporation of silicon, iron, and chromium, the chromium content being very small in the Φ- phase. The second-phase particles containing silicon, iron, and chromium are shown in Fig. 2. The microstructural characteristics of alloy 1 and 2 described above have a strong bearing on the corrosion resistance of alloys 1 and 2, as shown by polarization studies.
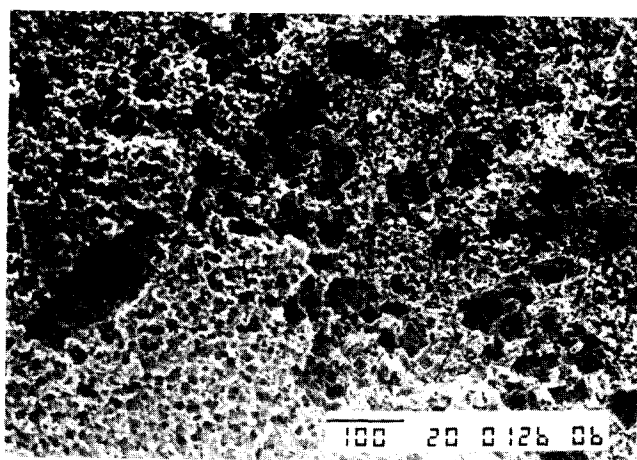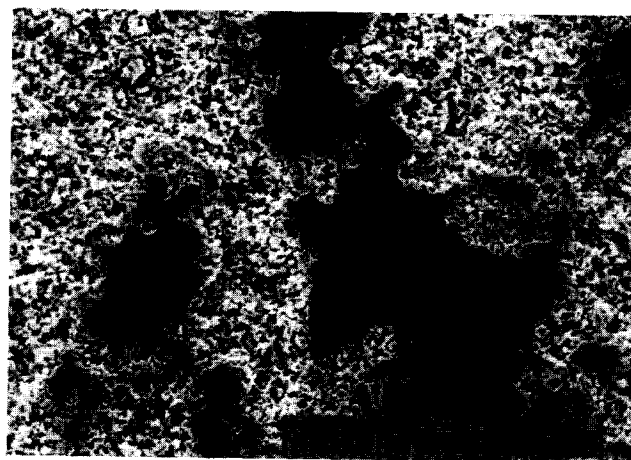
Typical polarization plots are shown in Fig. 3 and 4. On the basis of corrosion rates (mdd), the corrosion resistance of alloys 1 and 2 in decreasing order in Arabian Gulf water is as follows:

Alloy 1: T-6 > H-18 > O > T-4 > H-34
Alloy 2: O > H-18 > T-6 > T-4 > H-34

Table 3 Results of polarization studies in Arabian Gulf water

Temper	E, mV	β_a, mV/decade	β_c, mV/decade	I_{corr}, $\mu A/cm^2$	Corrosion rate, mdd
Alloy 1					
O	−751.0	56.65	−700.35	60.64	48.84
H-18	−730.0	68.06	−430.90	55.83	44.96
H-34	−723.0	52.50	−591.70	109.36	88.07
T-4	−761.0	52.17	−990.20	63.84	51.14
T-6	−758.0	47.10	−532.13	51.29	41.30
Alloy 2					
O	−762.8	373.43	−263.57	1.70	1.30
H-18	−818.7	117.24	−287.24	2.53	2.05
H-34	−769.0	123.30	−433.83	6.73	6.97
T-4	−742.61	285.90	−366.02	4.28	5.47
T-6	−779.03	289.45	−366.26	5.94	4.76

Fig. 8 Localized dissolution and pitting in alloy 2 (H-34 temper).

Fig. 9 Pitting and mild grain boundary attack in alloy 2 (O temper).

The difference between the corrosion rate of various tempers of alloy 1 and 2 is apparently due to the differences in the microstructure and alloy composition. The difference in the corrosion rate between the various tempers of the same alloy is due to microstructural changes induced by heat treatment.

In alloy 1, the least amount of corrosion (41.33 mdd) was shown by temper T-6 (solution treated at 525 °C for 30 min, water quenched, and artificially aged at 160 °C for 12 h). Temper T-4 (solution treated at 525 °C for 30 min, water quenched, and naturally aged to a stable condition) exhibits a higher rate of corrosion relative to T-6 (51.41 mdd). In artificial aging at 160 °C, the precipitates are evenly distributed, and the difference in potential between the solid solution and the precipitate is minimized, which retards localized corrosion in T-6 tempers. Figure 5 shows the dissolution of the grain boundaries and some intergranular attack in temper H-18 condition. Slight attack on the grain in a preferred orientation structure is shown in Fig. 6.

Alloy 1 in the H-18 temper (strain hardened by rolling) exhibits a substantially lower rate of corrosion (44.96 mdd) than H-34 temper (88.0 mdd). A network of precipitates in the H-34 tempers is shown in Fig. 7. The rate of corrosion appears to be

associated with the presence of a network of ΦAl_3Fe and Mg_2Si precipitates. Localized dissolution and pitting is pronounced in H-34, as shown in Fig. 8. Localized distribution of precipitates in the form of a network appears to enhance the corrosion rate of temper H-34. An intermediate rate of corrosion is exhibited by alloy 1 in the O temper (annealed). Figure 9 shows pitting and mild grain boundary attack in the O temper. Annealing appears to create areas of large potential difference between the solid solution and the second-phase precipitates, which causes localized dissolution. More detailed studies are required to establish the specific effects of microstructure on the rate of corrosion.

The corrosion resistance of alloy 2 is substantially higher than alloy 1. Chromium addition is primarily responsible for the improved resistance of alloy 2, because the remainder of the composition is not substantially different. The beneficial effect of chromium on the corrosion resistance of Al-Mg binary alloys has been previously reported.[13] The results of polarization studies of alloys 1 and 2 in Arabian Gulf water are shown in Table 3.

In alloy 2, chromium is present in finely dispersed C'-precipitates containing iron and magnesium.[14] Other phases pre-
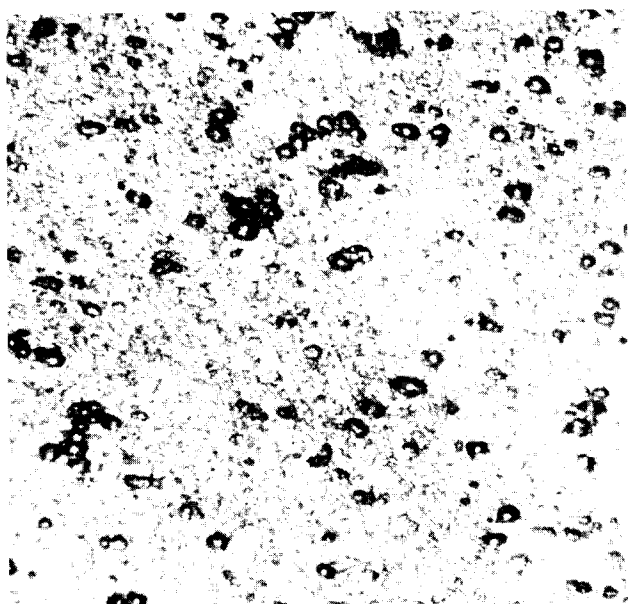
Fig. 10   Microstructure of alloy 2 in the O temper.

Fig. 11   Microstructure of alloy 2 in the H-18 temper.

sent are Mg_2 and ΦAl_3Fe. The structures of alloy 2 in O and H-18 tempers are shown in Fig. 10 and 11, respectively. The corrosion rate of the T-6 temper of alloy 2 (4.76 mdd) is lower than that of the T-4 temper, analogous to similar tempers of alloy 1. However, the rate of corrosion of the T-6 temper of alloy 2 is substantially lower than that of either the T-6 or T-4 tempers of alloy 1. It has been suggested that clusters of chromium are formed because of their low diffusivity, and they act as nuclei for collection of magnesium and silicon atoms.[15] Upon artificial aging, the solution atom becomes the nuclei for precipitates. Chromium reduces the width of the zones required for precipitation and minimizes the difference in the electrochemical potential between the solid solution and the precipitates. Chromium also promotes a more uniform distribution of precipitate within the grains.[16] Alloy in T-4 tempers does not exhibit improved corrosion resistance, which suggests that chromium does not have a beneficial influence on the corrosion resistance of an alloy if it is naturally aged after solution treatment at 525 °C for 30 min.

Alloy 2 in the H-34 temper exhibits a higher rate of corrosion compared to the H-18 temper. Of all the tempers investigated, high rates of corrosion were observed with the H-34 tempers of both alloys. The O temper in Alloy 2 exhibits a much higher resistance to corrosion in seawater than the O temper of alloy 1 because of the effect of chromium on control of grain size and recrystallization temperature during heat treatment and random distribution of precipitates.[17]

The investigations described above show that microstructural changes brought about by heat treatment have a significant effect on the corrosion resistance of modified aluminum-magnesium binary alloys in seawater. Because the modified Al-2.5Mg alloys are potential candidates for seawater service and desalination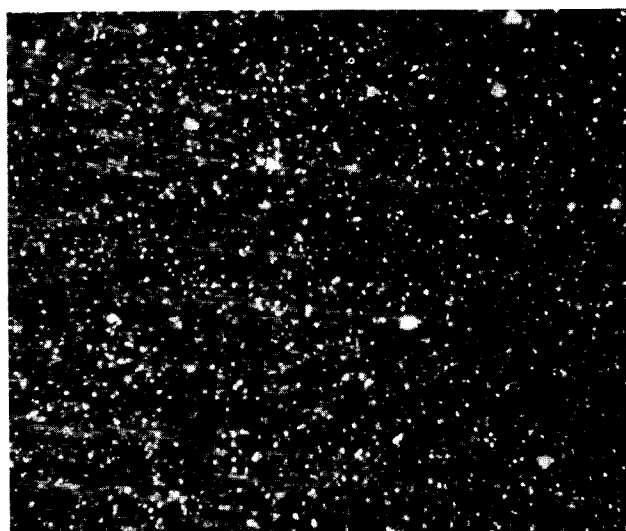, selection of an alloy must be based on a temper and alloying constituents that offer the highest resistance to corrosion.

4. Conclusions

On the basis of the results and discussions outlined above, the following conclusions are made. Alloy 1 in tempers O, H-18, H-34, T-4, and T-6 exhibits a higher rate of corrosion in seawater than alloy 2 in the same tempers. Chromium addition substantially improves the corrosion resistance of modified aluminum-magnesium binary alloys primarily by causing a more uniform distribution of precipitates within the grains and minimizing the difference in potential between the precipitate-free regions and the solid solution. Artificial age hardening at 160 °C improves the corrosion resistance of modified aluminum-magnesium alloys containing chromium. Temper designation is a vital consideration in the selection of modified aluminum-magnesium binary alloys for marine service and desalination plants.

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