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Investigation on influence of sodium- or strontium-modification on corrosion-resistance of Al–11.7%Si alloy

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Abstract Weight loss test in 4% sulfuric acid aqueous solution bath and salt spray test with 5% NaCl aqueous solution were used to evaluate the corrosion resistance of Al–11.7 wt%Si alloys with no modification, sodium modification, or strontium modification. SEM and optical microscopy were used to, respectively, observe the surface and depth corrosion morphologies of the alloys. The results showed that the corrosion-resistance of the alloy with no modification was the best, followed by the Sr-modified alloy, with the Na-modified alloy showing the worst results. Up to 360 h duration in 4% sulfuric acid aqueous solution bath, all the three alloys showed uniform corrosion characteristics. However, after 360 h duration, pitting corrosion became the typical characteristic of the modified alloys and it resulted in a considerable increase in percentage weight loss. After 480 h, the depth of the pitting holes in the Sr-modified alloy was larger than that in the Na-modified alloy, but the transverse corrosion channels in the former were far less than those in the latter. After this duration, the well-developed transverse corrosion channels in the Na-modified alloy became interconnected inch by inch, which led to severe exfoliation corrosion, so the percentage weight loss of the Na-modified alloy rose abruptly.

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Introduction

Due to their good mechanical properties, castability, weldability, and especially excellent corrosion-resistance, Al–Si casting alloys have been widely used in aerospace, ocean engineering, automobile and instrument engineering. Compared with A356 alloy, near-eutectic Al–Si casting alloys have much better castability, a smaller tendency for shrinkage voids, a more compacted structure and lower material costs. It attracts more and more attention of researchers [1–5]. Modification is one of the melt treatments generally carried out for Al–Si casting alloys, to enhance their mechanical properties, the purpose being to convert the morphology of the acicular brittle eutectic silicon particles observed in the non-modified alloy to a fine fibrous form that enhances the alloy properties, in particular, the ductility. Sodium is the strongest modifying element, and has been widely used in Al–Si casting alloys. But the control of sodium-modification is quite difficult due to its well-known rapid oxidation and the undesirable effect of over-modification. It is also unfriendly to the environment. Strontium is the preferred modifier in current use. Addition of strontium in the near-eutectic Al–Si alloy not only results in a modification of the eutectic silicon, but also an obvious increase in the amount of α-Al dendrites and promotion of columnar growth of these dendrites, increasing both the strength and ductility of the alloy considerably [6, 7].

Aluminum alloys have excellent resistance to corrosion, due to the formation of a passivating oxide film on their surface. The corrosion of aluminum alloys can be uniform as well as local. The existence of weak points in the surface oxide layer commonly causes the development of local corrosion cells, active-passive cells. Such defects may be due to inhomogeneities in the composition, slag inclusions, precipitates of secondary phases or casting defects of the alloys. The local corrosion of aluminum alloys presents itself mainly in the form of pitting corrosion, intercrystalline corrosion, exfoliation corrosion and stress corrosion cracking. Pitting corrosion occurs very commonly on the surface of aluminum alloys in tap water, wet atmosphere, weak acid solutions or salt solutions. The origin of pits is controlled by the existence of the defects. At these sites, corrosion proceeds at a higher rate than it does on the remainder of the passive surface. The high corrosion current at these sites leads to a local increase in the surface salt concentration as a result of transport processes (migration and diffusion) and anion adsorption on the electrode. The high surface concentration of anions displaces the water molecules from the double layer and thus suppresses the passivation reaction and simultaneously promotes oxide film dissolution. As a result of these processes, the film thickness decreases and the electric field across it increases. Under the action of a high electric field, anions penetrate into the oxide film. The density of the lattice defects increases and, together with the high electric field, increases the ionic conductivity of the oxide layer. The latter loses its passivating properties and is transformed into a non-passivating oxide, which is able to sustain high corrosion current densities.

Since most parts of aluminum alloys have to be exposed to an aggressive environment, many researches on corrosion and protection of these alloys have been carried out, focused however on wrought aluminum alloys such as the 7××× [8–10], 2×××[11], 6×××[12] and 5×××[13–14] series alloys. A new corrosion-resistant casting aluminum alloy (Al–Mg–Si) has been reported, however, its castability is far less than that of Al–Si casting alloys [15]. The latter are the most widely used casting aluminum alloys, but research on the corrosion-resistance aspects of the alloy is scant. It has not been established whether modification has or does not have an influence on the corrosion-resistance of Al–Si casting alloys. In this study, salt spray and weight loss tests were carried out on non-modified and Na- and Sr-modified Al–11.7%Si alloys to investigate the influence of modification on the corrosion-resistance. The results obtained are presented and discussed in this article.

Experimental procedures

Preparation of the corrosion sheets of Al–11.7%Si alloys

The experimental alloy charge was a commercial alader ingot with a normal composition of Al–11.7%Si–0.2%Fe. Melting with 3 kg ingot for every alloy was carried out using a 5 kW electrical resistance crucible furnace. NiCr–NiSi thermocouples and a WZK-1 controller were used to control the temperature of the melts. After melting at 760 °C, the melts were cooled down to 730 °C, and then degassed with a SR-WJ1 degassing agent using a 0.3% addition of the melt by weight for about 5 min. Alloy1 as named was not modified, and Alloy 2 was modified by a salt flux addition (60NaF + 25NaCl + 15KCl), and Alloy 3 was modified using a Al–10%Sr master alloy where the melt was stirred slightly by hand for about three minutes and was held for an additional 30 min. The melts were poured at 720 °C into a cast iron mold with a cavity of $200 \times 150 \times 10\ \mathrm{mm}^3$, which was preheated at 250 °C. Thirty standard corrosion sheets ($50 \times 25 \times 3\ \mathrm{mm}^3$) of the three alloys were machined from the castings respectively, which were then mechanically polished and marked by number. From previous experience, 0.5% of the melt weight of Na salt flux or 1% of the melt weight of Al–10Sr master alloy were used in order to achieve the targeted Na level (90 ppm) and Sr level (300 ppm) in the melts. However, under the current addition conditions, the Na and Sr levels achieved in the alloys were 80 and 290 ppm, respectively. The compositions of the three alloys were determined using ICP-spectroscopy, as listed in Table 1.

Salt spray test with 5%NaCl aqueous solution

One sheet of each alloy was used in the salt spray test, working in accordance with the National Standard of China (GJB4.11-83) specifications. A solution of NaCl at about 5% by weight (50 ± 5 g/L) and at a pH of 6.8 was used. This solution was prepared by dissolving NaCl of analytical purity in de-ioned water and adjusting the pH with NaOH and HCl solutions of analytical purity. A FY-03 spraying cabin was used, in which the temperature was 35 ± 2 °C, the pressure 101.325 kPa and the total population of solid particles was less than 20 ppm during testing. The deposition rate of the salt solution was $0.02\ \mathrm{mL/h\ cm}^2$. After

Table 1 Composition of three alloys

Alloys	Concentrations in the alloys				Addition level by weight of the melt, wt%	
	Si (wt%)	Fe (wt%)	Na (ppm)	Sr (ppm)	Na salt flux	Al–10Sr master alloy
Alloy 1	11.68	0.19	<10	<10	–	–
Alloy 2	11.75	0.22	80	<10	0.5	–
Alloy 3	11.72	0.19	<10	290	–	1.0

spraying continuously for 120 h duration, the sheets were removed from the cabin and washed with plenty of distilled water.

Weight loss test in 4% sulfuric acid aqueous solution

Twenty sheets of each alloy were used in the weight loss test in 4% sulfuric acid aqueous solution bath at a temperature of 25 ± 2 °C. The 4% sulfuric acid aqueous solution was confected with sulfuric acid of analytical purity and de-ioned water. Prior to the weight loss test, these sheets were cleaned in an ultrasonic bath of acetone, followed by hot air drying, and then immediately weighed using an electronic analytical balance with a sensitivity of 0.1 mg, to record the original weight, W_{or}. Then, the sheets of the three alloys were hung above the bath at the same time, dipped to the same depth of 35 mm. Four sheets of each alloy were taken out simultaneously after durations of 120, 240, 360, 480 and 600 h, respectively. The corrosion products on the surfaces of the sheets were removed by immersing the sheets in HNO_3 at 70% for 2 min, followed by rinsing in an ultrasonic bath of acetone and hot air drying, and then weighed to give the corroded weight, W_{co}. The weight loss percent was defined as $(W_{or} - W_{co})/W_{or} \times 100\%$. Each data point was obtained from the mean of four sheets.

Microstructural observations

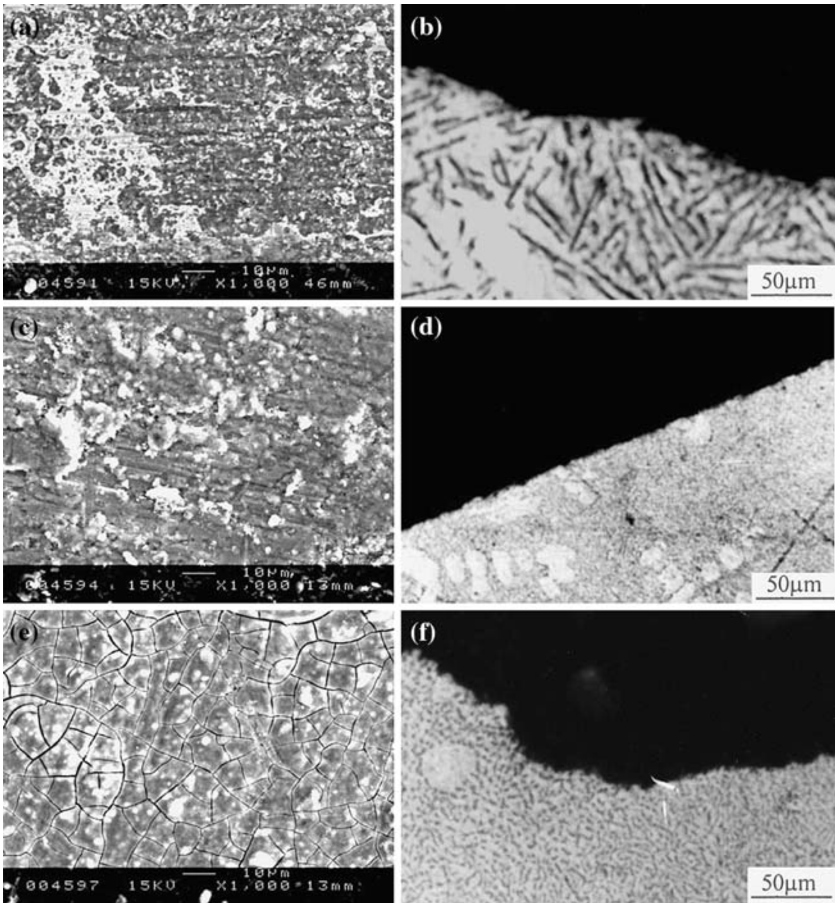
Metallographic samples, cut from the middle parts of the three alloys castings, were mechanically polished and then etched with Keller's reagent. An optical microscope (OLYMPUS BX-60M) was used to observe the microstructures. Both a sheet obtained from the weight loss test of 480 h duration which had been cleaned with HNO_3 and a sheet obtained directly from the salt spray test of 120 h duration were cut, respectively, into two small parts with surface areas of 10×10 mm^2. One of these was used directly to observe the surface corrosion using scanning electron microscopy. The other, mounted in epoxy as a metallographic sample, was used to examine/determine the depth of corrosion (along the thickness direction of the sheet) by optical microscopy. The small sheet obtained from the salt spray test was immersed in HNO_3 to remove corrosion products prior to mounting for metallographic examination.

Results and discussion

Figure 1 shows the surface and depth corrosion photographs of the non-modified, Sr-modified and Na-modified Al–11.7%Si alloy samples. After the salt spray corrosion test of 120 h duration, a small amount of corrosion was observed on the surface of the unmodified alloy sheet sample (Fig. 1a) and the Sr-modified alloy sample (Fig. 1c), with visible corrosion crannies found on the surface of the latter. However, the surface of the Na-modified alloy sample was overlaid with a thick film of corroded products and the corrosion crannies were interconnected in the form of a mesh (Fig. 1e). After the corroded products were eliminated, the corrosion depth of the alloys was examined. The corroded surfaces of both the unmodified and Sr-modified alloys were level, as shown in Fig. 1b, d, respectively, however, the surface of the Na-modified alloy became severely dented (seen as in Fig. 1f) after only 120 h. The results above indicate that the corrosion-resistance of the unmodified and Sr-modified alloys in neutral salt medium for a short duration is equivalent, by and large, but far less in the case of the Na-modified alloy.

Figure 2 shows the different trends of the weight loss percent in the three Al–11.7%Si alloys with duration time in 4% sulfuric acid aqueous solution bath. A slight increase in weight loss is observed with increase in time up to 360 h, with no considerable difference between the three alloys. After 480 h, the weight loss percent in the Na-modified and Sr-modified alloys (11.25% and 9.52%, respectively) was remarkably larger than that in the unmodified alloy (6.00%). At 600 h, the weight loss of the Na-modified alloy was 42.91%, far larger than that of the Sr-modified alloy (13.63%) and the unmodified alloy (6.10%). From the curves of weight loss percent versus duration time shown in Fig. 2, it can been seen that modification leads to a considerable increase in the corrosion rate

Fig. 1 SEM (**a**, **c**, **e**) and optical (**b**, **d**, **f**) micrographs showing surface and depth corrosion in Al–11.7%Si alloy in the non-modified (**a**, **b**), Sr-modified (**c**, **d**) and Na-modified (**e**, **f**) conditions, after a salt spray corrosion test of 120 h duration, using 5% sodium chloride aqueous solution



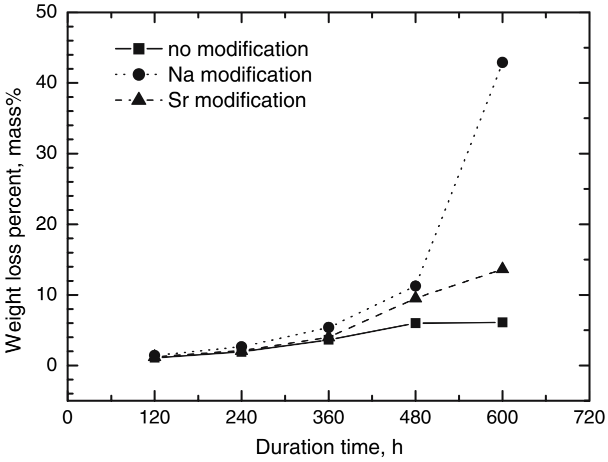


Fig. 2 Weight loss percent versus duration time of Al–11.7%Si alloys with no modification (■), sodium modification (●) or strontium modification (▲) in 4% sulfuric acid aqueous solution bath

(weight loss per unit time) of the modified alloys after 360 h, and the corrosion rate of the Na-modified alloy rose abruptly after 480 h. The results of the weight loss test indicate that in strong acid aqueous solution the unmodified alloy has a good corrosion resistance, strontium modification decreases the corrosion resistance somewhat, where as sodium modification leads to a severe decrease. This point is important for the application of Al–Si casting alloys.

Figure 3 shows the representative surface and depth corrosion photographs of Al–11.7%Si alloys with no modification, strontium modification or sodium modification, after 480 h duration in 4% sulfuric acid aqueous solution bath. The surface of the non-modified alloy sheet was relatively smooth, and large pitting was not observed even though a small quantity of corroded spots (about 50–70 μm depth) were present, as seen in Fig. 3a, b. It was rational to think that the chemical reaction occurred uniformly over the whole surface. That is to say, the corrosion mode in the non-modified alloy is uniform. Modification resulted in a considerable change of the corrosion mode of the alloy, where pitting was the main characteristic. These pittings were large and deep, and originated at weak points on the surface of the sheet, penetrating in the direction of depth and transversely at the same time, and resulting in a ‘‘tree-like fibrous’’ corroded morphology as seen in

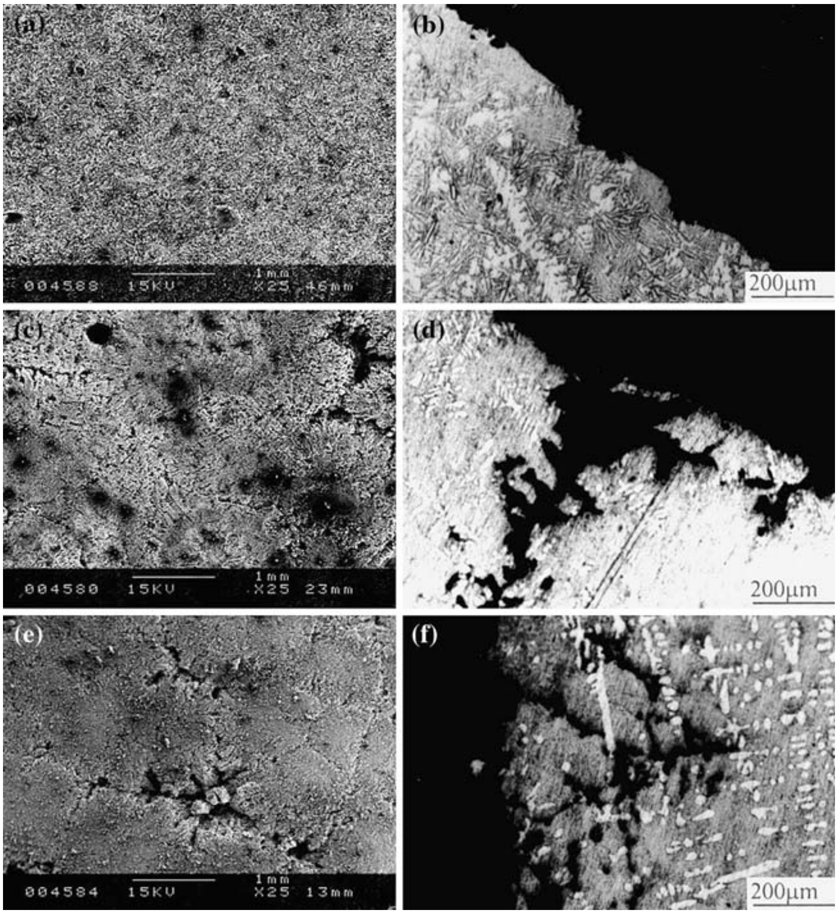


Fig. 3 SEM (**a**, **c**, **e**) and optical (**b**, **d**, **f**) micrographs showing surface and depth corrosion in Al–11.7%Si alloy in the non-modified (**a**, **b**), Sr-modified (**c**, **d**) and Na-modified (**e**, **f**) conditions, in 4% sulfuric acid aqueous solution bath for 480 h duration

Fig. 3c–f. The corrosion channels penetrated through the eutectic zone, but the α-Al dendrites were observed to be less attacked (Fig. 3f), suggesting that the corrosion resistance of the α-Al dendrites was better than that of the eutectic.

There were differences in the corrosion morphology of the Na- and Sr-modified alloy sheets. Pits on the surface of the Na-modified alloy were larger in size (Fig. 3e). On the surface of the Sr-modified alloy sheet, a small number of corroded holes with transverse corrosion channels (originating from the pitting hole, approximately perpendicular to its depth direction), as seen in Fig. 3c, d. The transverse corrosion channels in the Na-modified alloy were far more developed, and had a tendency to interconnect, as seen in Fig. 3e, f. The depth of the corroded holes in the Sr-modified alloy (>800 μm) was larger than that in the Na-modified alloy (about 600 μm). The difference in the corrosion morphology between the Na- and Sr-modified alloys may be related to the orientation of the α-Al dendrites in these alloys.

In the non-modified alloy, the eutectic silicon crystals were present as flakes and the orientation of the coarse α-Al dendrites was disordered (Fig. 4a). Modification resulted in changing the morphology of the eutectic silicon particles from flake-like to fibrous, and however, the size of the silicon fibers in the Sr-modified alloy was much finer than that in the Na-modified alloy (Fig. 4b, c). More of interest is the α-Al dendrites. The amount of α-Al dendrites in the Na-modified alloy was not increased and the orientation of them was also disorder (Fig. 4b). However, in the Sr-modified alloy, the amount of α-Al dendrites was increased observably, and, more of importance, the orientation of them was orderly (Fig. 4c), consistent with the direction of heat flow during solidification, and the secondary dendrite arms were refined obviously. The schematic of orientation of α-Al dendrites in Na- or Sr-modified Al–11.7%Si alloys was shown in Fig. 5. The difference in microstructure between these alloys could have an influence on the corrosion resistance.

Strontium could promote the columnar growth of the α-Al dendrites in Al–Si casting alloy [7]. In the Sr-modified alloy, the orientation of the α-Al dendrites paralleled the direction of heat flow, that is, the direction of thickness of the casting. During dipping in

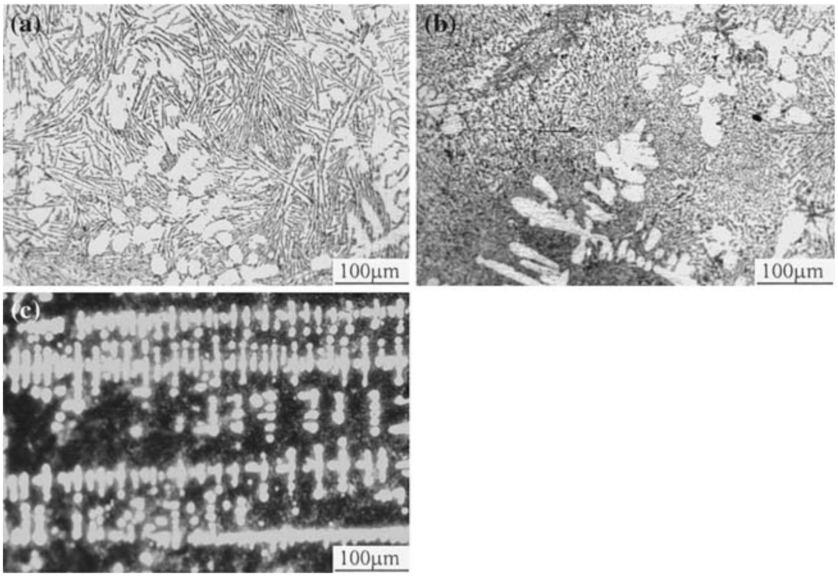


Fig. 4 Optical micrographs showing the microstructures of (**a**) non-modified, (**b**) Na-modified, and (**c**) Sr-modified Al–11.7%Si alloys

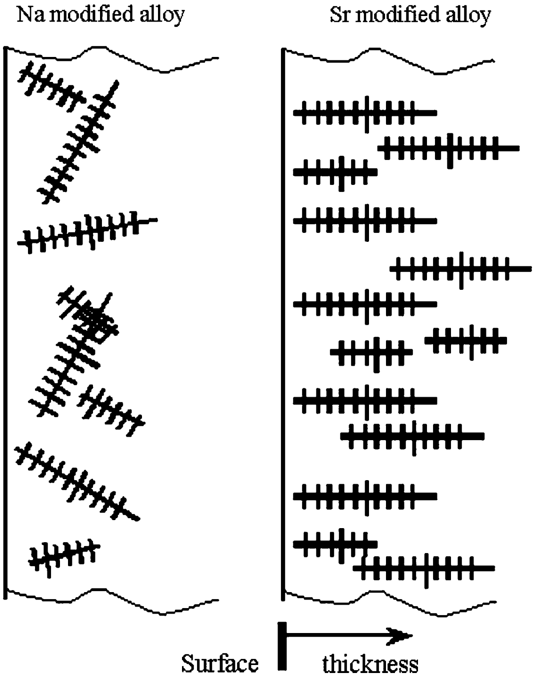


Fig. 5 Schematic diagram showing orientation of α-Al dendrites in Na- and Sr-modified Al–11.7%Si alloys

strong acid solution, the pitting on the surface pushed ahead in the direction of thickness of the sheet. That is to say, the developing direction of the pitting depth was consistent with the orientation of the α-Al dendrites in the Sr-modified alloy. The transverse penetration of corrosion channels was severely restricted by the ordered orientation of the dendrites in this alloy and due to their better corrosion resistance compared to the eutectic, so the transverse corrosion channels were not well developed. But, in the Na-modified alloy, the disordered orientation of the α-Al dendrites favored the transverse penetration of corrosion channels, resulting in transverse corrosion channels that were far more developed. Even though both the Na- and Sr-modified alloys exhibited the same basic corrosion characteristic, i.e. pitting corrosion, after 480 h, this difference in corrosion channels between them determined their different weight loss behaviors.

The electrical potential of silicon is –0.26 V, and that of aluminum is –0.85, and that of α-Al with 1% Si in solid solution is –0.81V. The difference in electrical potential between Al and Si is so much that it is rational to expect that the alloy may be corroded quickly. However, silicon is passivated due to the formation of an oxide film on the surface of the Al–Si alloy sheet, so that it is inert in most corrosive media [16]. When the sheet of the non-modified Al–11.7%Si alloy was immersed in the sulfuric acid solution, a passivated film was quickly formed on the surface. The weight loss that resulted was the consequence of the competition between the formation and dissolution of the passivated film. The passivated film formed on the surface of the non-modified alloy was stable, protecting the alloy from further corrosion. Even though its dissolution was accelerated after 360 h, the film was not broken, thus maintaining its corrosion resistance. The formation of pitting in the unmodified alloy seemed to be difficult, as seen from Figure 3a, b. It is well known that in order for a pitting attack to occur on a metal surface, a certain minimum corrosion potential, the so-called pitting or break-through potential, must be attained. From the results of Figs. 2 and 3a, b, it was rational to think that the pitting potential was not attained for the unmodified alloy during the test durations studied, so uniform corrosion (general corrosion) was the main mode of corrosion. For the Na- or Sr-modified alloys, the corrosion mode up to 360 h was also mainly uniform corrosion, as same as in the non-modified alloy. Due to the protection of the passivated film, the weight loss was small, increasing only slightly with time. Some shrinkage pores and micropores were observed in the microstructure of the Na-modified alloy, as seen in Fig. 4b. These defects were easily susceptible to pitting, so the weight loss in the Na-modified alloy after 360 h was somewhat larger that of the non-modified and Sr-modified alloys. The presence of sodium or strontium in Al–11.6%Si alloy not only changes the morphology of the eutectic silicon particles, but may also decrease the pitting potential. Thus, after 360 h, the pitting potential in the modified alloys could be easily attained and a subsequent local dissolution of the oxide film could occur at a weak point. As soon as a pit formed, it would continue to grow autocatalytically, creating conditions that promoted further growth. Consequently, pitting corrosion became the typical mode of corrosion in the modified alloys. Shrinkage porosity and micropores in the microstructure of the Na-modified alloy might promote the formation and development of the transverse corrosion channels. The development of the pitting caused the corrosion accelerated, so the weight loss percent of the modified alloys was increased considerably after 360 h. For the Sr-modified alloy, most of the corroded holes were isolated from each other, with few transverse corrosion channels. The corroded holes pushed ahead in the depth direction and broadened all around, so the corrosion rate of the alloy maintained a certain level after 360 h, larger, however, than that of the unmodified alloy. But, for the Na-modified alloy, not only did the corroded holes push ahead, but the transverse corrosion channels also developed rapidly. With the progress of corrosion, the transverse corrosion channels tended to interconnect, resulting in the removal of small parts of the metal from the sheet body (i.e., exfoliation corrosion), and hence the corrosion rate increased rapidly, leading to the abrupt rise in weight loss observed in the Na-modified alloy after 480 h.

Conclusions

The salt spray test indicated that the corrosion-resistance of the non-modified and Sr-modified Al–11.7%Si alloys in neutral salt medium for a short duration was equivalent, by and large, while that of the Na-modified alloy was far less. The weight loss test in strong acid solution showed that non-modified alloy had the best corrosion-resistance, followed by the Sr-modified alloy, with the Na-modified alloy showing the least corrosion resistance. Up to 360 h testing in 4% sulfuric acid aqueous solution, all the three alloys exhibited uniform corrosion characteristics. However, after 360 h, pitting corrosion became the typical corrosion mode in the modified alloys. The depth of the pitting holes after 480 h testing was larger in the Sr-modified alloy than that in Na-modified alloy, but the transverse corrosion channels in Sr-modified alloy were far fewer in comparison. In addition, after 480 h, the well-developed transverse corrosion channels in the Na-modified alloy interconnected progressively, leading to severe exfoliation corrosion.

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