

Corrosion Behavior of Twin-Roll Cast Al-Mg and Al-Mg-Si Alloys

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Abstract

AlMg and AlMgSi alloys are used for automotive applications, where a good corrosion resistance is required. Recently, there has been a growing interest in using strip casting as a method to produce low-cost aluminum sheet for automotive applications. The present work was undertaken to investigate the corrosion behavior of twin-roll cast AA5754 and AA6016 sheet for panel applications, on the basis of electrochemical pitting experiments and intergranular corrosion tests. The passivity breakdown (pitting) behavior and repassivation of the pits of twin roll cast AA5754 and AA6016 sheet were investigated using potentiodynamic polarization techniques in neutral solutions containing chloride ions.

1. Introduction

While lighter weight is the primary reason for selecting aluminum for body applications, outstanding corrosion performance provides an additional advantage that is highly important in extending the useful life of a vehicle [1,2]. Aluminum has a highly protective barrier oxide film on its surface which forms instantaneously and, if damaged, reforms immediately in most environments. Hence, aluminum does not rust away on exposure to the environment even under severe conditions resisting corrosion by water and road salt. This excellent corrosion performance and durability of aluminum in automotive applications has been confirmed by the field experience that has been gained in sports and luxury cars. While aluminum sheet is technically very attractive, its high cost has always been a concern for the car manufacturer. Hence, twin roll casting has recently been offered as a method to produce low-cost aluminum sheet for body applications. The twin-roll cast 5XXX and 6XXX alloys were shown to be at least equivalent to their DC-cast counterparts [3,4]. The present work was undertaken to investigate the corrosion behavior of twin roll cast AA5754 and AA6016 sheet on the basis of electrochemical pitting experiments and intergranular immersion tests.

2. Experimental

Table 1 The chemical composition of the Al-Mg and Al-Mg-Si alloys used in the present investigation (%wt).

alloy	Si	Fe	Mg	Mn	Cu	Cr	Ti	Al
5754	0.113	0.292	3.072	0.213	0.027	0.001	0.021	96.23
6016	1.002	0.189	0.429	0.073	0.003	0.001	0.028	98.25

The AA 5754 and 6016 alloys used in the present investigation were both strip-cast at ASSAN Aluminum in the gauge range of 5-6mm. The chemical composition of the strips are given in Table 1. 5754 cast strip was cold rolled to an intermediate gauge (4.5mm) where the sheet was soaked at 450°C for 8 hours. It was then cold rolled to the final gauge of 1mm and given a softening anneal at 350°C. The 6016 strip, on the other hand, was cold rolled on an industrial scale to the final gauge of 1mm. 1mm thick sheet thus obtained was solutionized at 550°C for 30 minutes at Marmara Research Center. The solutionized samples were cooled in circulating air and were then pre-aged (T4P). The pre-aged sheet samples were held at room temperature for one week before they were given the paint-bake treatment (T8X treatment).

The 5754 and 6016 sheet samples thus produced were subjected to cyclic polarization experiments in a 0.1 N NaCl solution at room temperature to investigate their pitting behavior. An EG&G PARC M 273 model galvanostat/potentiostat was employed and the applied potential was varied at a scanning rate of 5 mV/min. The solution of 0,1 N NaCl was purged with pure nitrogen for 45 minutes before each experiment in order to clean away the dissolved oxygen. 30 minutes was allowed after the immersion of the specimen into the solution in order for the corrosion potential to stabilize. The applied potential scan was reversed to the corrosion potential once the current density reached 400 μ A/cm², in order to examine the repassivation of the corrosion pits. The samples were ground with 800 grade emery paper and then degreased in acetone prior to experiments. Open circuit potentials of the samples in the same solution but open to air were recorded as a function of time for 30 min. Immersion test was employed to determine the corrosion rate of sheet samples in 3,5 % NaCl solution at room temperature. Sheet samples of 25x25 mm were cut, polished and degreased in acetone prior to testing. The samples were removed from the solution after 475 hours. Corrosion products were removed with 50% aqueous solution of nitric acid. Average corrosion rates were estimated from weight loss measurements. The susceptibility to intergranular corrosion (IGC) of the two alloys was tested using the "Nitric Acid Mass Loss Test" (NAML or weight loss; ASTM G 67-93). The samples were immersed in concentrated nitric acid at room temperature for 24 h following surface pretreatments in 5% NaOH at 80°C and desmutting in nitric acid.

3. Results and Discussion

Results of the electrochemical cyclic polarization (ECP) experiments, open circuit corrosion potential (OCP) measurements, immersion and intergranular corrosion tests are listed in Table 2 for the two alloys investigated in the present work. The 6016 alloy reveal more noble pitting (E_{pit}) and repassivation potentials (E_{rp}) in the ECP experiments, but a larger repassivation hysteresis loop than the 5754 alloy (Figure 1) suggesting that the two alloys may have different pit morphologies, populations, size and/or pit repassivation rates etc. Microscopic observations showed that randomly distributed crystallographic pits have formed in both alloys (Figure 2), with no evidence of alkaline pits produced by intermetallic cathodes

Table 2: Results of the electrochemical cyclic polarization experiments, immersion and IGC tests.

Alloy	Electrochemical Cyclic Polarization			Number & size of pits	Immersion Test		IGC Test
	$E_{op\ cir}$	E_{pit}	E_{rp}		weight loss (mg/cm ²)	Number of pits	weight loss (mg/cm ²)
	(mV vs SCE)						
5754	-700	-725	-770	Low & large & shallow	8,1	low	0,411
6016	-625	-610	-665	High & small	10,4	high	0,412

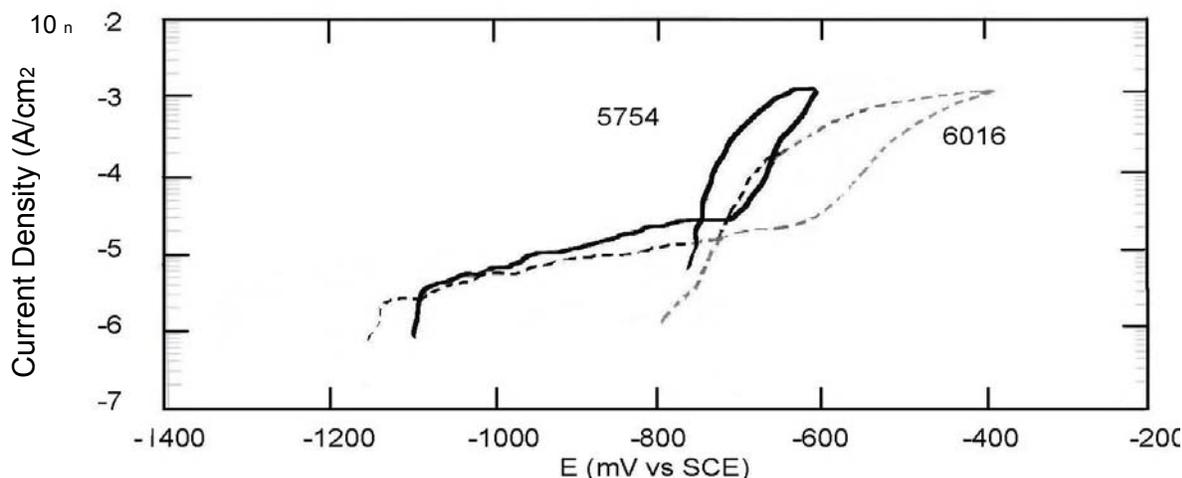


Figure 1: Cyclic polarization curves of 5754 and 6016 alloys in 0,1 N NaCl solutions at room temperature.

in either sample [5]. The pits in the 6016 alloy, however, were smaller and more in number while fewer but larger yet shallower pits have formed in the 5754 alloy. This is believed to be why the hysteresis loop was larger in the former. With a more noble pitting potential and smaller pits, the pitting initiation and pit propagation resistance of the 6016 alloy appear to be notably higher than those of the 5754 alloy.

In spite of a more noble E_{pit} , the 6016 alloy revealed higher weight loss after 472 days of immersion in 3,5% NaCl solution. A higher number of pits have formed in the 6016 alloy in immersion tests as in the case of ECP experiments (Figure 3) with no evidence of crystallographic pits this time. Residues of intermetallic particles identified in most pits in both alloys suggest that the formation of these pits might have been governed by intermetallic particles in the immersion test. With a higher weight loss and higher pit population for the 6016 alloy, the results of the immersion test seem to contrast those of the ECP experiments. Pitting initiates, in an ECP experiment, at E_{pit} , the critical pitting potential at which anodic current increases sharply [6]. E_{pit} merely marks the onset of pitting but does not relate to the extent of pit initiation nor to the propagation of freshly initiated pits. Hence, an alloy with a more noble pitting potential may suffer a higher weight loss in an immersion test owing to a higher number of pits, thus a larger hysteresis loop in the ECP experiment.

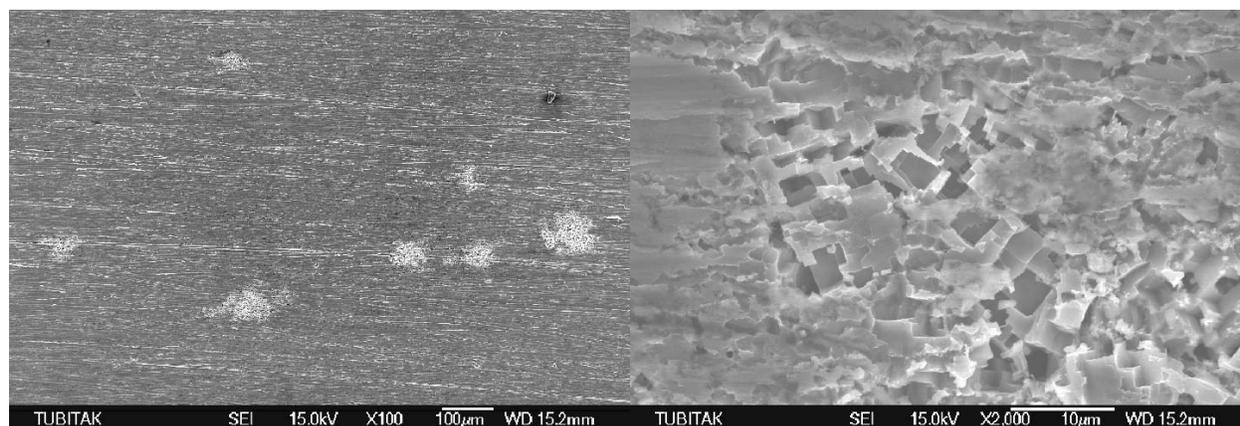


Figure 2: A typical pit distribution (a) and crystallographic pit morphologies (b) of the investigated alloys.

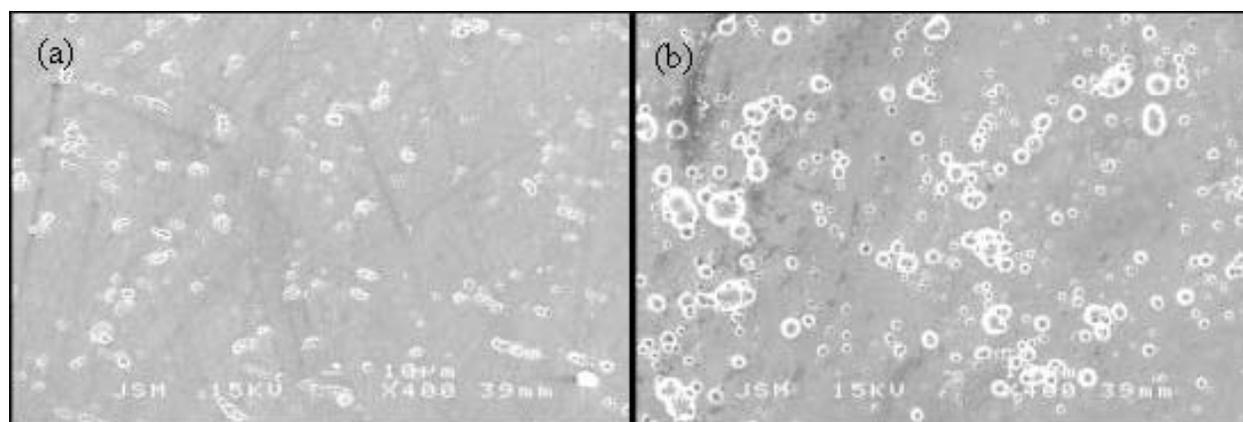


Figure 3: The samples after immersion test in 3,5 % NaCl solution: (a) 5754, (b) 6016.

OCPs of the two alloys were recorded as a function of time for 30 minutes in order to identify the origin of crystallographic pits formed in the ECP experiments. The samples were subsequently examined by SEM to find out if there were freshly initiated pits. OCPs of the two alloys shifted in the more noble direction for a while and then stabilized near the pitting potentials of the respective alloys obtained in the ECP experiments (Figure 4). Time to stabilization of OCP was longer for the 6016 alloy (approx. 210 s for 6016 alloy and 100 s for 5754 alloy). SEM examinations after OCP measurements revealed newly initiated pitting sites after 30 minutes in neutral 0,1 N NaCl solution containing oxygen. This indicates that pits have already nucleated below E_{pit} during corrosion potential stabilization before ECP experiment. Moreover, these newly initiated sites were of different morphologies; crystallographic, alkaline and mixed ones (Figure 5). Most of the alkaline pits in the 6016 alloy were observed to have formed around AlFe(Mn)Si particles, while they were around Al-Fe(Mn) particles in the 5754 alloy. The occurrence of three different morphologies suggests that some particles might have served as initiation sites leading to early growth into the matrix through crystallographic tunnels [7] forming crystallographic pit morphologies in the propagation stage. This is believed to be why no alkaline pits were observed after ECP experiments as the pits have already grown to be crystallographic in the propagation stage. The intermetallic particles apparently play a critical role in pit initiation of both alloys in ECP experiments as well as in immersion tests. The number of pits initiated is clearly linked to the population and type of intermetallic particles in both test methods.

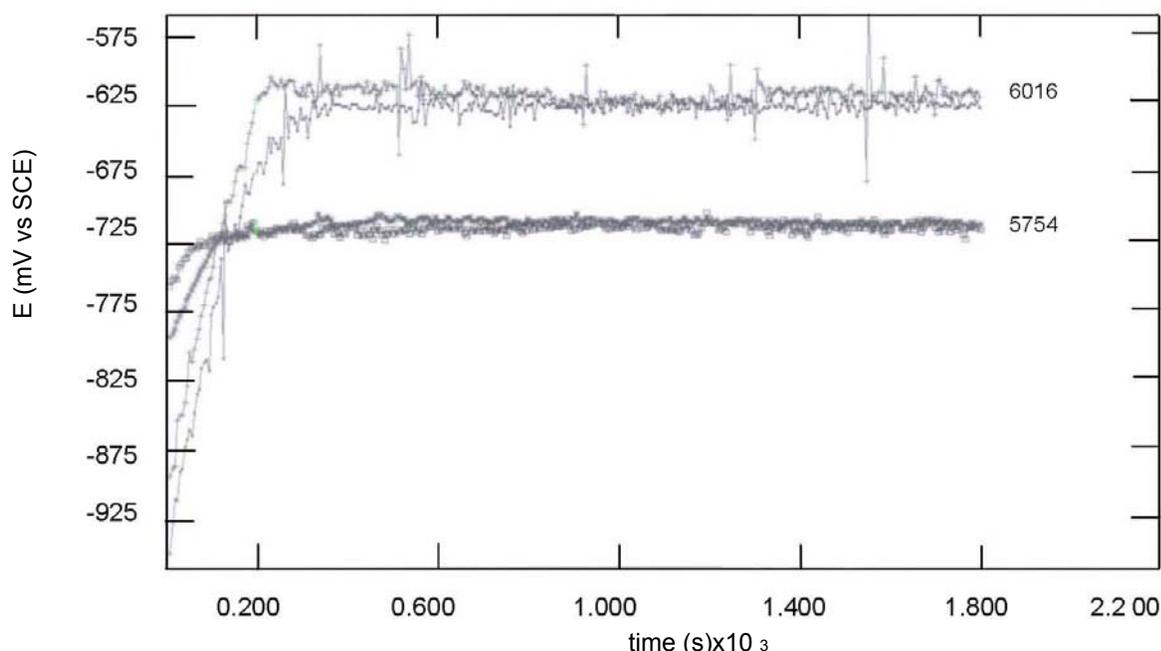


Figure 4: Open circuit potential vs time graphics of 5754 and 6016 sheet samples in 0.1 N NaCl solutions open to air at room temperature.

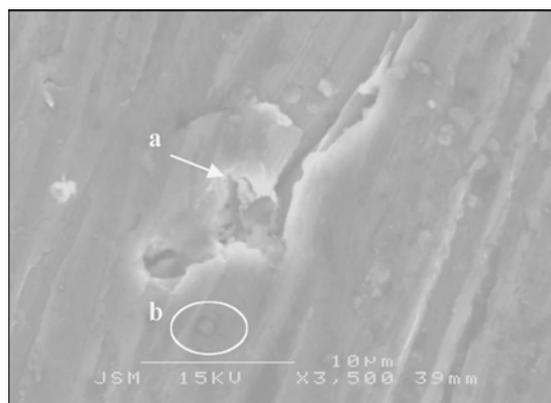


Figure 5: Freshly formed crystallographic pits (a) and alkaline pit initiation sites (b) after open circuit potential measurement in 0.1 N NaCl solution.

The two alloys have different type, number density and distribution of intermetallic particles. The population of the particles was much higher in the 6016 alloy than in the 5754 alloy (Figure 6). The majority of the particles in the latter were identified by SEM-EDS to be $Al_6(Fe,Mn)$ type with relatively few Mg_2Si particles. Some of the $Al_6(Fe,Mn)$ particles also contained Cu. The 6016 alloy, on the other hand, was dominated by $AlFe(Mn)Si$ particles with a Fe/Si ratio close to 1. The matrix compositions of the two alloys were also different. Much of the Mg in the 5754 alloy was in solution while the matrix in the 6016 alloy, was largely depleted of Si and other alloying elements.

It is well known that Fe-bearing particles are more noble with respect to the aluminum matrix and have an adverse effect on the localized corrosion resistance of aluminum alloys depending on their Mn and/or Si content [8,9,10]. The most harmful ones are known to be of the Al_3Fe variety while $Al_6(Fe,Mn)$ and $AlFe(Mn)Si$ particles are less detrimental owing to their Mn and Si content. Mn and Si reduce cathodic current density decreasing the galvanic effect between the matrix and the particle and their galvanic actions with the matrix ($\alpha-Al$) are similar. Hence, it is not fair to link the poor pitting resistance of the 5754 alloy to the $Al_6(Fe,Mn)$ particles, although they also contain some Cu. The corrosion potential of the matrix in Al alloys is known to depend on the solute content [9,10]. With a much higher Mg in solution, the corrosion potential of the matrix in 5754 is likely to be more negative than that of the 6016 alloy in 0,1 N NaCl solution. The galvanic effect between $Al_6(Fe,Mn)$ particles and

the matrix would thus increase giving a lower pitting initiation resistance in the former. The AlFe(Mn)Si intermetallic particles in the 6016 alloy present lower cathodic activity due to their Si content and lower galvanic action with the matrix owing to lower solute levels thus retarding pit initiation. Mg₂Si particles were probably not active in pitting initiation since they have nearly the same corrosion potential with the aluminum matrix [11], with no galvanic effect between the two.

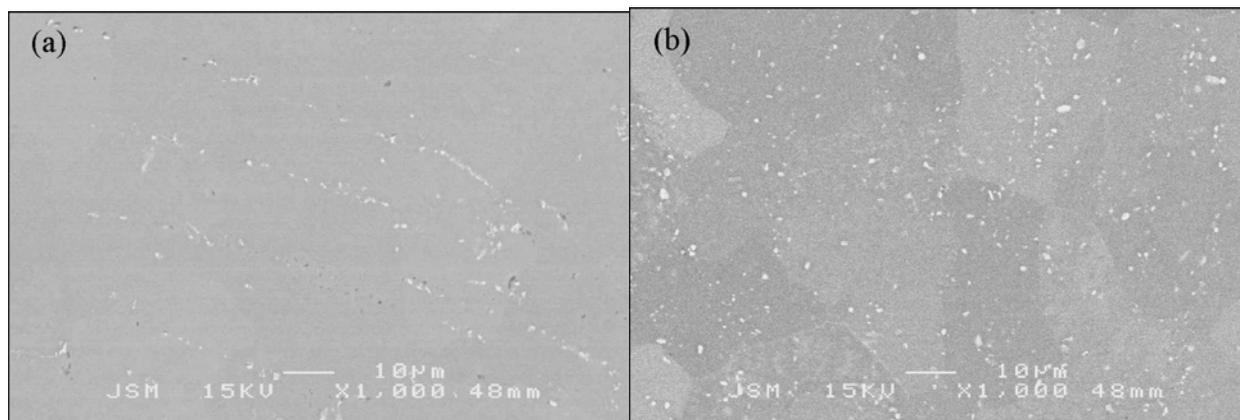


Figure 6: Particle characteristics of the a) 5754, b) 6016 alloys

Al-Mg alloys with more than 3 % Mg are known to be susceptible to intergranular corrosion. So, the intergranular corrosion behavior of the 5754 alloy was investigated. The 6016 sheet samples were also submitted to the same test for the sake of comparison. The weight loss measurements on samples immersed in a concentrated nitric acid for 24 h are given in Table 2. There is hardly any difference between the weight loss values of the two alloys. According to ASTM G 67-93, for any alloy to be identified as susceptible to intergranular corrosion, weight loss values should be in the range of 30 to 44 mg/cm², while the range is from 1 to 8 mg/cm² for a resistant alloy. It is thus fair to conclude that the 5754 and 6016 alloys used in the present investigation are resistant to intergranular corrosion with very low weight loss values ranging from 0,399 to 0,412 mg/cm².

4. Conclusions

Localized corrosion behavior of TRC 6016 and 5754 sheet alloys were compared. The 6016 alloy is more resistant to pitting corrosion than the 5754 alloy. Small but a higher population of pits have formed on the surface of the 6016 alloy, while coarser but fewer pits were observed in the case of 5754 alloy giving lower weight loss in the immersion test for the latter. After open circuit potential measurement, newly initiated pitting sites were observed in both alloys. These pits were crystallographic, alkaline type and of mixed type in terms of morphology. Alkaline type pits were initiated around AlFe particles in 5754 alloy and around AlFeSi particles in 6016 alloy. Both alloys were found to be highly resistant to intergranular corrosion.

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References

- [1] K. Mizuno, A. Nylund, I. Olefjord, Corrosion Science 43, 381-396, 2001.
- [2] ASM Handbook – Volume 13 “Corrosion”, 6th Edition, 1998.
- [3] Y. Birol, G. Zeybekoglu, G. Kara, M. Dunder, O. Cakır, A. Akkurt, G. Yıldızbayrak, C. Romanowski, Automotive Alloys 2001, edited by S.K. Das, The Minerals, Metals & Materials Society, 107, 2001.
- [4] Y. Birol, to be published in Z. Metallkunde.
- [5] A. Aballe *et al*, Corr. Science 43, 1657-1674, 2001.
- [6] D. Jones, Principles and Prevention of Corrosion, Mcmillan Publishing Company, 209, 1992.
- [7] V. Guillaumin, G. Mankowski, Corr. Science 42, 105-125, 2000.
- [8] K. Nisancioglu J. Electrochem. Soc., 137, 69-77, 1990.
- [9] O. Lunder and K. Nisancioglu Corr. Science 44, 414-422, 1988.
- [10] M. Zamin, Corrosion, 37, 627, 1981.
- [11] W. Zust, Proc. Int. Conf. Aluminium 2003, 129-134, 2003.