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Comparison of the Corrosion Behaviors of Twin-Roll Cast and DC Cast AA 6016 and AA6082 for Automotive Applications

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Abstract

Recent studies conducted on continuosly cast 6000 series alloys showed that microstructural features and mechanical performances of these materials exhibit very satisfactory results. These features have to be supported by other material characteristics, such as general corrosion behavior in order to be competitive against steel and even the Direct Chill(DC) cast-hot rolled equivalents. In the present study we aimed to study and make comparison between the corrosion behaviors of DC and Twin Roll Cast(TRC) 6000 series aluminum alloys. Pitting and micro galvanic corrosion of DC and TRC samples were tested and evaluated. Cyclic Voltametry(CV) experiments and salt spray tests were employed to determine their pitting and micro galvanic corrosion behaviors. The corrosion behavior is discussed by considering the surface macro and microstructural features of the samples. The results revealed the importance of surface segregation on corrosion performance.

1. Introduction

There has been recently a growing demand for producing more fuel-efficient, that is, light-weight vehicles in order to reduce the energy consumption and air pollution. High strength-to-stiffness ratio, good formability, good corrosion resistance and recyclability potential are considered as general characteristics of aluminum which therefore can meet the weight reduction demands of the market.

For the time being, 5xxx series aluminum alloys are preferred for inner panel applications. On the other hand, age-hardenable 6xxx series alloys are used for outer panels. The strength after the paint-bake process together with the good formability supply the optimum conditions for outer sheet material applications.

Another considerable purpose of the automotive industry, other than reducing fuel consumption and pollution, is to reduce the production cost. The production technique could be considered as one of the main cost determining factor. When compared to direct chill (DC) cast aluminum, twin roll cast (TRC) alumimum has lower production costs stemming from less number of downstreaming processes. DC cast aluminum products are successfully being used for inner and outer panel and heat shield applications in automotive industry. Therefore, there is no reason for TRC aluminum products, having compatible formability, corrosion and welding properties with those of DC products, not becoming the reason of choice because of their cost efficient nature.
As far as corrosion properties of aluminum alloys are concerned, there exists a considerable amount of published studies [1-4]. In wrought aluminum alloys the resistance to pitting corrosion are found to be in the following order 1xxx, 5xxx, 3xxx, 6xxx, 7xxx and 2xxx [5]. The intermetallics character and morphology play a key role in the pitting corrosion of Al alloys. Depending on their composition, intermetallics can act as micro cathodic, anodic or neutral sites. In 6XXX Al alloys intermetallics are mainly composed of Fe,Si,Mn and Mg. The presence of Fe in those intermetallics makes them to behave as cathodes[6].
Although there are substantial number of studies concerning the pitting behavior of DC cast 6XXX series alloys, we found only one study in the literature related to the corrosion of TRC aluminum alloys[7].
Present study has been conducted in order to reveal the differences in corrosion behaviours of DC and TRC 6016 and 6082 aluminum sheet products. Salt spray tests were performed and pitting/repassivation potentials were determined by using cyclic anodic polarization curves. The results of the experimental studies are evaluated and related to the microstructure of the alloys, namely the intermetallic size and distribution. The results have been discussed in light of the studies concentrated on the effects of intermetallic types, sizes and density on the corrosion behaviour of aluminum alloys.

2. Experimental Procedure

DC and TRC 6016 and 6082 alloys were used in this work. TRC samples were supplied by ASSAN Aluminum,Turkey. The heat treatment of the specimens were performed by AMAG Rolling Gmbh, Austria. The chemical compositions of 2 mm thick DC and TRC cast aluminum alloy specimens in T4 temper are given in Table 1.

Table 1. The chemical compositions of DC and TRC specimens.

Specimen Designation	Si (wt%)	Fe (wt%)	Cu (wt%)	Mn (wt%)	Mg (wt%)	Cr (wt%)	Zn (wt%)	Al (wt%)
6016 DC	1.124	0.162	0.078	0.069	0.374	0.003	0.019	98.12
6016TRC	1.126	0.22	0.080	0.062	0.390	0.002	0.006	98.07
6082 DC	0.91	0.432	0.077	0.482	0.836	0.025	0.049	97.12
6082TRC	0.908	0.382	0.005	0.466	0.769	0.002	0.006	97.42

The samples were ground with SiC paper, polished with 3 μm diamond suspension and finished with colloidal silica. Prior to the polarization experiments the sample surfaces were cleaned with acetone, alcohol and rinsed with deionized water as stated by ASTM G5 standard. 5%wt NaCl was used as an electrolyte. VoltaLab 40 type potentiostat was used to conduct all polarization experiments.

Polarization experiments were carried out in an electrochemical cell with five inlets. A graphite and a saturated calomel electrode was used as a counter and reference electrodes, respectively. The potential of the reference electrode is -241 mV vs NHE. The electrolyte was deaerated by purging high purity nitrogen gas. Nitrogen was introduced to the system starting from an hour earlier than the beginning of the experiment and continued to be sent throughout experiment. Anodic polarization measurements were performed starting from open circuit potential(OCP) with a 0.16 mV/s sweep rate. When the current density reached 1 mA/cm², scanning was reversed in order to study the repassivation behavior.

The critical pitting potential marks the transition from passivation to pitting and is typically determined by locating the onset of the rapidly rising current during an anodic polarization scan through extrapolation to the baseline current of the passivation region. We refer to the value obtained by this method as E_{pit}. On the other hand, the repassivation potential which we will refer here as Erp, marks the transition from pitting to passivation on the reverse scan during cyclic voltammetry. Alloys held well below the critical pitting potential display a steadily increasing current with time until E_{pit}. Beyond E_{pit} the value of the current increases exponentially indicating the pitting initiation and propagation. The pitting and repassivation potentials determined using the aformentioned method are tabulated in Table 2.

Prior to salt spray tests (SStest), the specimens were cleaned in acetone ultrasonically for 10 minutes. No special surface preperation were employed. SStests were performed under 5.0 %wt NaCl solution for 48 hours at 35°C with alternating 15 minutes of salt spraying and 45 minutes of waiting time periods. After the tests were performed, the specimens were cleaned with alcohol and protected for further investigation.

Following cyclic anodic polarization and the SStests , the surfaces and the cross-sections of the samples were examined using JEOL JSM-5600 type scanning electron microscope and when necessary semi–quantitative chemical analysis were performed by utilizing the EDS facility attached to SEM.

3. Results

Electrochemical Results

The critical pitting and repassivation potentials determined from CV responses of the alloys investigated in this study are tabulated in Table 2. Figures 1 and 2 show the anodic polarization behavior of top and cross-sectioned surfaces of both DC and TRC cast 6016 and 6082 alloys in 5%wt NaCl, respectively.

DC cast samples have much wider hysteresis loops and more electropositive(noble) pitting and repassivation potentials compared to those of TRC samples. No significant effect of alloy composition has been observed on the pitting behavior (Figure 1).

It is known that the surface structure of TRC samples differs substantially from the bulk. A typical microstructure of a TRC sample showing the intermetallic sizes and distribution difference between the surface and the bulk is shown in Figure 3. The intermetalics within a shallow depth of the strip(100-200 µm) from the surface are more in number and smaller in size compared to the bulk In order to see the bulk pitting behavior and compare it with DC samples, anodic polarization tests were also conducted on the cross sections of the samples. In this case the pitting and repassivation potentials and hysteresis width of the samples did not show any significant difference (Figure 2). These results clearly indicated the important role of surface structure of TRC samples on the pitting corrosion behavior.

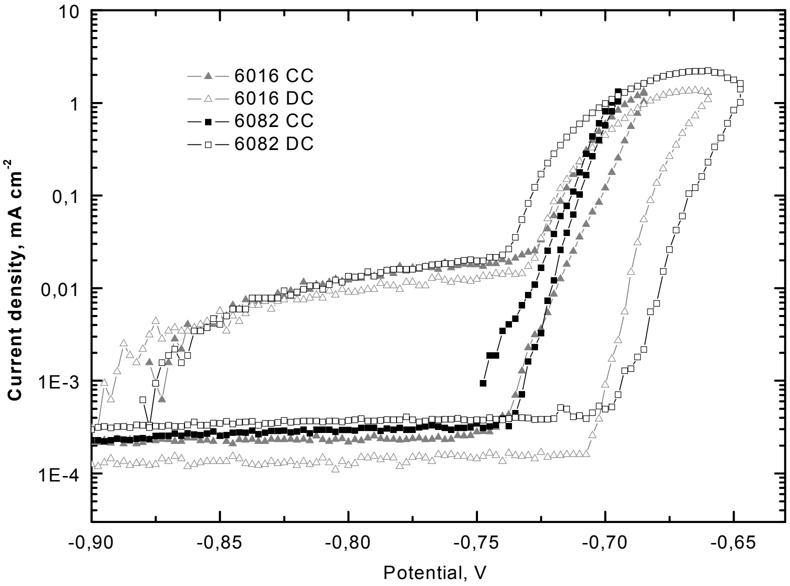

Figure 1. Potential dynamic scans of TRC and DC 6016 and 6082 aluminum alloys in 5%wt NaCl. Scan rate = 0.16 mV/sec. (Top surfaces)

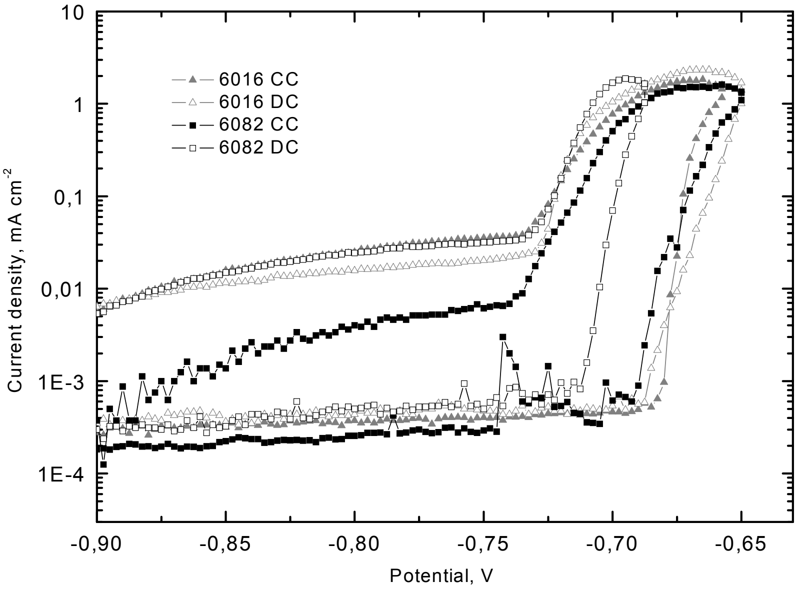

Figure 2. Potential dynamic scans of TRC and DC 6016 and 6082 aluminum alloys in 5%wt NaCl. Scan rate = 0.16 mV/sec.(cross-sectioned surfaces)

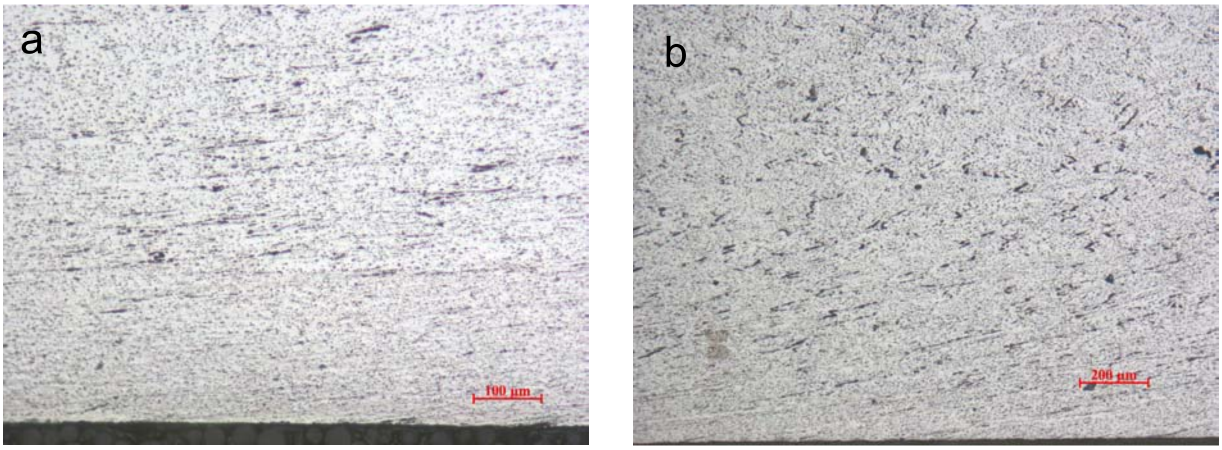

Figure 3. Typical cross-section microstrucutre of a) 6016 TRC and b) 6082 TRC samples

Morphology After Anodic Polarization Experiments

The surface morphologies of the samples (top and transverse) whose polarization data were given in Figures 1 and 2 respectively were examined and shown in Figure 4. .

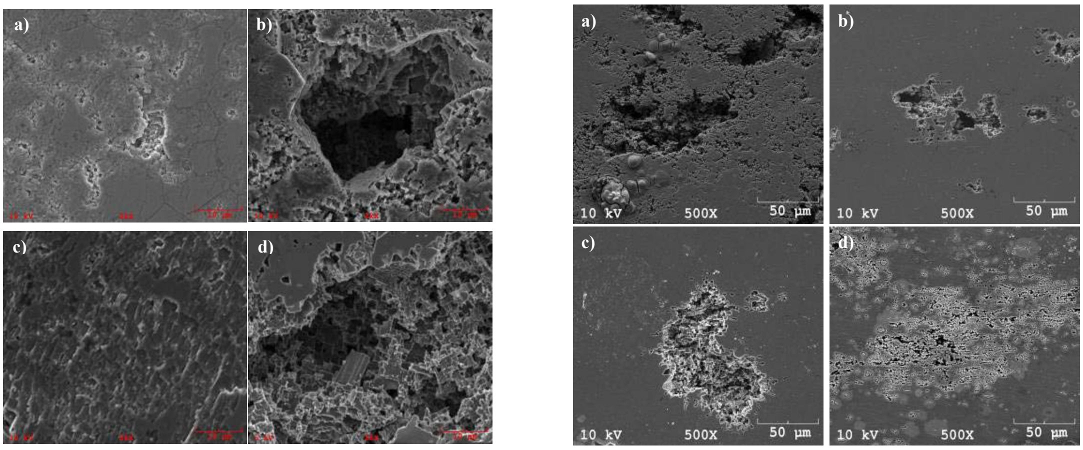

Figure 4. SEM images of the top(left) and transverse(right) surfaces after anodic polarization. a) Al 6016 TRC, b)Al 6016 DC, c)Al 6082 TRC ve d)Al 6082 DC.

The difference in pit morphologies between the top and cross-sectioned surfaces is clearly seen from the figures. While the pit morphologies observed on DC cast samples were much larger, deeper and less in number, those observed on TRC samples were smaller, shallower and more in number which resulted in the easier repassivation of the alloy surfaces hence narrower hysteresis loops. This pitting morphology at the cross-sectioned surface on the other hand changes when we look at the SEM images on the right. The pit morphologies on TRC samples resemble to DC counterpart. This change in the pitting morphology agrees well with the polarization data (Figure 1 and 2).

Table 2. Pitting and repassivation potentials determined from cyclic polarization curves for the top(Figure1) and cross-sectioned surfaces(Figure2).

Alloy	E_p , mV	E_{pp} , mV	$E_p - E_{pp}$, mV
6016 DC	- 707	- 732	25
6016 TRC	- 745	- 737	8
6082 DC	- 700	- 740	40
6082 TRC	- 735	- 747	8
Pitting and repassivation potentials extracted from cyclic polarization curves(Figure 2) for the alloy surfaces but cut into cross section.			
6016 DC	- 687	- 730	43
6016 TRC	- 685	- 735	50
6082 DC	- 712	- 735	23
6082 TRC	- 692	- 740	48

Morphology After Salt Spray Test

In terms of visual inspection of the surfaces(Figure 5), in general terms complying with the results of the anodic polarization tests, numerous homogeneously distributed shallow pits were observed on TRC samples. On the other hand, there are countable numbers of wide pits on DC cast samples. Both 6082 TRC and DC samples showed better corrosion performance when compared to their counterparts. Interestingly, this difference was not observed in anodic polarization experiments. The detailed investigation of the surface morphology after SStest was performed using SEM.

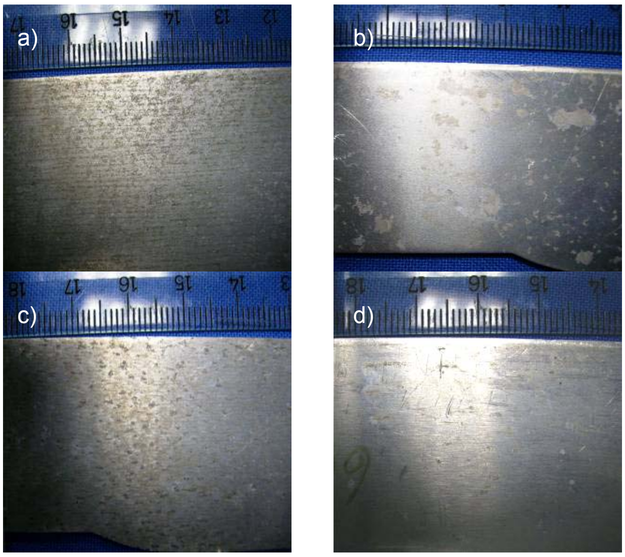

Figure 5. Digital camera images of the surfaces after Sstest performed for 2 days in aerated solution of 5%wt NaCl a)Al 6016 TRC, b)Al 6016 DC, c)Al 6082 TRC ve d)Al 6082 DC

A surface layer of corrosion products was observed on both DC and TRC sample surfaces after the salt spray test (Figure 6). The coverage of this layer was more substantial on TRC samples highly probably due to the large number of small pits on the surface.

Two types of pit morphologies are observed on both DC and TRC sample surfaces; 1) alkaline pits that are formed around cathodic intermetallics 2) crystallographic pits.

On DC samples, alkaline pits are larger due to coarser intermetallics (Figure 6 b,d). The analysis of the retained intermetallics in the pits mainly contain Al, Fe, Mn and Si (Figure 7); or contain Al, Fe, and Si(Figure 8). Hence they are cathodic in character. Similar but far smaller alkaline pits are also observed on TRC samples. However due to their small sizes (0.2-1 mikron) it was not possible to determine their composition with the available analysis techniques (Figures 6 a,c).

Numerous hemispherical cavities of variety of sizes on both DC and TRC alloy surfaces observed in the micrographs are created highly probably by the disappearance of the intermetallics, simply by detachment from the surface. The presence of metallic inclusions more noble than the matrix reduces the resistance of the alloy to corrosion. Since these intermetallics are more noble i.e cathodic compared to the surrounding Al matrix, dissolution of the less noble Al matrix around the precipitates results in the formation of isolated pits and detachment of the intermetallic eventually.

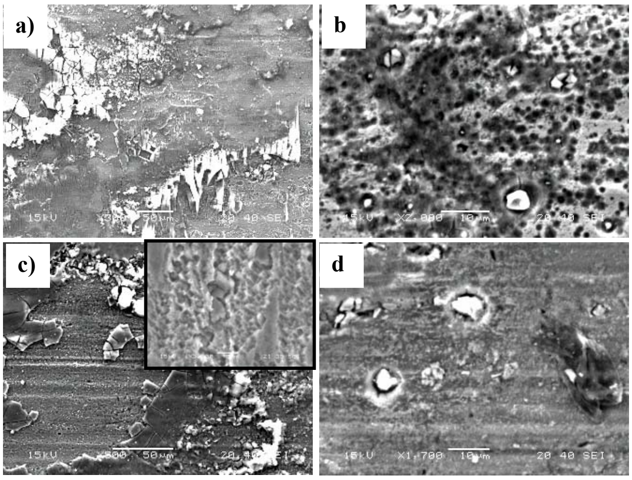

Figure 6. SEM micrographs of the top surfaces of a) Al 6016 TRC, b)Al 6016 DC, c)Al 6082 TRC ve d)Al 6082 DC after salt spray test at 5 %wt NaCl.

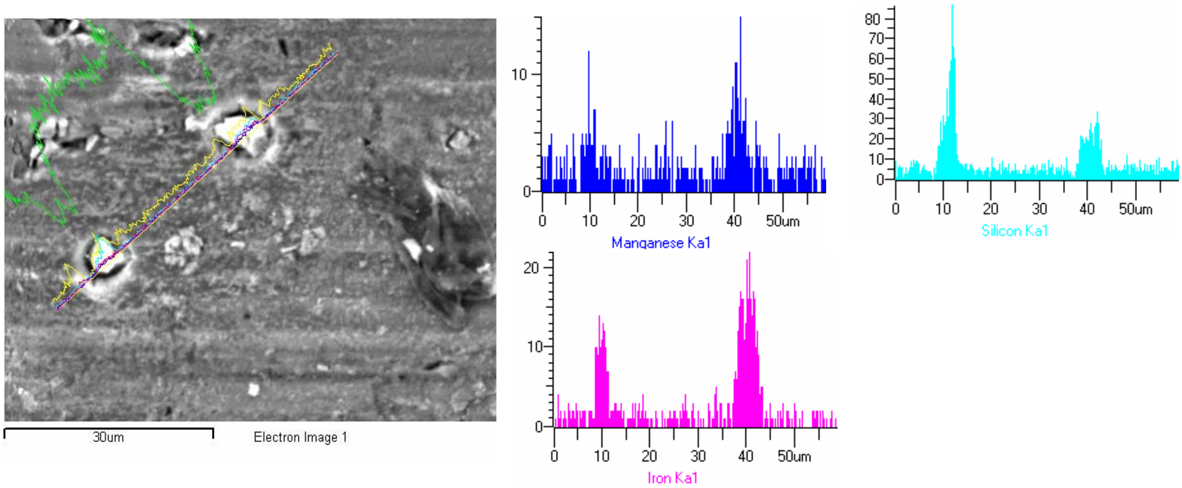

Figure 7. EDS spectrum analysis on the intermetallics AlFe(Mn,Si) observed on 6082 DC cast top surface(fig.6(d))

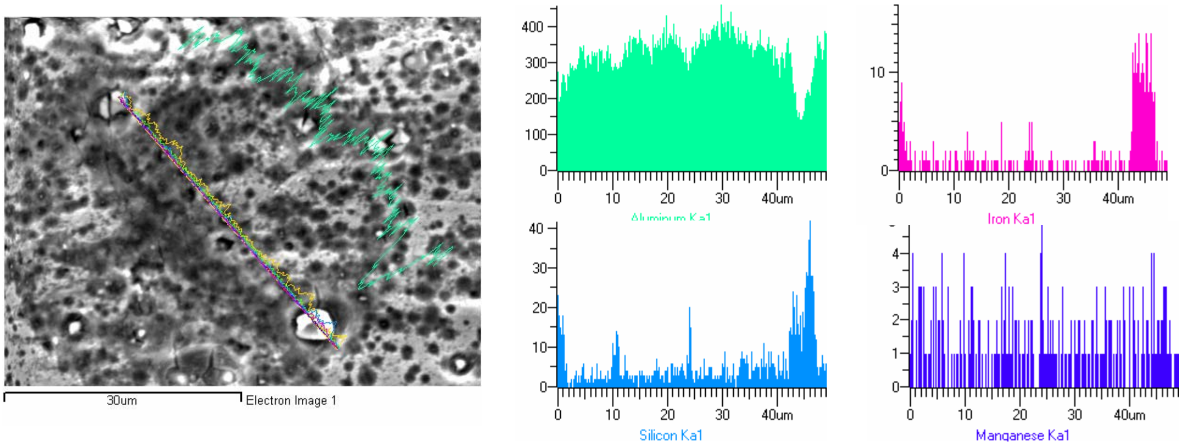

Figure 8. EDS spectrum analysis on the intermetallics Al(Fe,Si) observed on 6082 DC cast top surface(fig.6(b))

4. Discussion

The results of the experiments conducted within the scope of the study revealed the importance of microstructure on the pitting behaviour of aluminum alloys. TRC aluminum has different microstructure than that of DC cast materials. Water cooled caster rolls provide very high solidification rates (upto 800 ^{0}C/sec). Rapidly solidified outer skin, featureless zone, has a supersaturated microstructure with very fine grains and large number of small sized intermetallics decorating this limited volume. The thickness of this volume ranges from 50-150 mikrons. The effect of this structure is clearly reflected to the electrochemical corrosion behavior and to the morphology of the pits formed on these surfaces. It is found that the pitting potentials of TRC specimens are more negative than those of DC specimens. The more negative pitting potentials can be attributed to the nature of TRC technique resulting in segregation on the surface which, in turn, weaken the naturally occuring oxide layer and serve as preferable sites for pit initiation. The high number and small shallow pits on TRC samples can be explained by the presence of small sized cathodic intermetallics on the supersaturated surface zone. This morphology is not observed on the bulk of TRC samples indicating the specificity of this pitting morpholgy to the supersaturated surface zone. The SStests also verified these results. Moreover it was possible to differentiate more clearly the effect of composition on the pitting behavior of these alloys. Alloys with higher Mn content, namely 6082 series exhibited better corrosion behavior regardless of their processing technique. These results showed the positive effect of Mn on the cathodic character of the intermetallics as indicated in other studies in the literature[6,8-9].

5. Conclusions

1. It was found that the pitting potentials of DC cast specimens are more positive than those of TRC specimens. The more negative pitting potential values could be attributed to the nature of TRC technique causing segregation on the surface which, in turn, weaken the naturally occuring oxide layer and serve as preferential sites for pit initiation.

2. Although specimens produced by TRC technique have more negative pitting potentials when compared to those of DC cast specimens, they repassivated more quickly when compared to DC specimens which leads to a narrow hysterysis. Implication of a narrow hysterysis is that the formed pits are getting passivated before they get bigger and deeper. Even though narrow hysterysis is affirmative in terms of corrosion behavior, large number of pits present an

unacceptable aesthetic apperance. Cyclic anodic polarization curves conducted on the cross-sectioned surfaces of TRC samples on the other hand exhibited a similar hysteresis to that of DC cast samples.

3. Salt spray tests results agress well with those obtained from the cyclic anodic polarization data. After salt spray tests, surfaces of DC cast specimens remained shiny and exhibited a few number of pits , while TRC cast specimen surfaces reveal large number of pit formation. But in SStests the positive effect of Mn on the pitting behavior is more clearly exhibited.

4. As the results are evaluted by taking the alloy types into consideration, it can be deduced that there exist no significant differences between the pitting potentials. According to the salt spray test results, it is possible to say that 6082 alloys, independent of the production technique, are more resistant to pitting and this behaviour could be attributed to the presence of Mn.

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