

# Influence of Malonic Acid on SCC Behaviour of Anodic Coated Al-Alloys 1050

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## Abstract

This paper presents results from a study of stress corrosion cracking behaviour of Al-Alloy 1050 anodised in a 3M H<sub>2</sub>SO<sub>4</sub> anodising bath in the presence of malonic acid in various concentrations. Crack formation and propagation evaluation were undertaken during SCC tests using constant load tests. The influence of applied potential on SCC behaviour was also examined. The SCC behaviour of anodised Al-Alloy 1050 was observed to vary with malonic acid concentration, applied potential and stress level. All prepared coatings protected the bare alloy, with better protective properties in the case of 0.015 concentration of malonic acid. Coatings prepared in these conditions had better mechanical properties as indicated from the increased resistance to SCC at a high stress level, than coatings prepared in other conditions of malonic acid concentration. Also in this case, crack formation and propagation was slower and observed cracks and local corrosion phenomena were fewer in number and smaller in size than in all other case. Prepared coatings were observed to increase protective properties in an area of applied potentials slightly more anodic than the free corrosion potential values.

**Keywords:** SCC, Protection, Aluminium, Anodic Coatings, Malonic Acid.

## Introduction

The SCC behaviour of Al-alloys of the 1XXX series is rarely studied because the high strength Al-alloys, eg. the 7XXX series are more important for most industrial applications. Nevertheless, Al-alloys of the 1XXX series are widely used in many commercial applications and therefore studies of these alloys are useful for estimating the effects of the various constituents of high strength alloys on their corrosion behaviour.

Studies on behaviour of pure aluminium in saline environments and in stress corrosion conditions, concluded that, in common with other Al-Alloys, cracking is due to the absorption of atomic hydrogen absorption, which promotes crack growth and increases dislocation activity. Also, depending on the applied potential, different processes may

predominate and the SCC at open circuit potential (OCP) is caused by pit formation and crack initiation at pits, Trueba [1], Braun [2], Zhu [3].

Some Al-alloys used in practice, are anodically oxidised, for protection against corrosion and SCC. It has been shown that during anodising, a porous  $\text{Al}_2\text{O}_3$  film with a cellular structure up to a thickness of 36  $\mu\text{m}$  is formed, with cells oriented parallel to the direction of gravity this resulting from the rapid evolution of oxygen in the opposite direction. It was observed that the protective properties of oxides change with thickness and structure, being better against corrosion than aluminium but worse against mechanical stress, Skoulikidis [4-6].

Many studies, Popovits [7], Ozyilmaz [8], Breslin [9], Galkowski [10], Trabelsi [11], Grandfield [12], Chattopadhyay [13], report the effect of the addition of various organic compounds on the corrosion behaviour of metals, mainly in the corrosive environment, but also, as in the case of aluminium, can be in the anodising bath during the electrolytic preparation of the oxides. The explanation given for this effect is the absorption of compounds on the metal surface or the formation of some complexes on it. It is also known the use of coatings systems containing a wide variety of polymeric compounds with the presence of various other additives, metals, oxides, clays, nanocomposites, Kouloumbi [14], Patil [15], Yu [16], Souza [17].

In earlier works, Spathis [18-20] the effect on corrosion and stress corrosion cracking behaviour of anodised 1050 Al-Alloy of the addition in an anodising bath of 3M or 4M  $\text{H}_2\text{SO}_4$  of some inorganic compounds, bicarboxylic acids in 3M  $\text{H}_2\text{SO}_4$  or carboxylic acids in 4M  $\text{H}_2\text{SO}_4$  was examined. From the results of these works followed that the better protective properties against corrosion and SCC showed the anodic coatings prepared in an anodising bath of 3M  $\text{H}_2\text{SO}_4$  with an addition of malonic acid.

In order to further investigate this effect, aim of the present work is the study of stress corrosion cracking behaviour of 1050 Al-Alloy anodised in a 3M  $\text{H}_2\text{SO}_4$  anodising bath with the presence in it of malonic acid in various concentrations. The investigation was carried out by SCC tests. Crack formation and propagation during SCC tests was studied and the influence of applied potential on SCC behaviour was also examined.

## Experimental

Tests were conducted on Al-Alloy 1050 and the corrosive environment was a 3M NaCl solution.

### Anodising conditions

The anodic coatings on Al-Alloy surface were prepared electrolytically in a bath of 3M H<sub>2</sub>SO<sub>4</sub> with an addition of various concentrations (0.005M - 0.1M) of malonic acid. The anodising current density was 6 A.dm<sup>-2</sup>, at 25°C and the coatings thickness was estimated to 10 µm. The true thickness of the coatings was confirmed by direct microscopy examination of cross sections from the anodised specimens.

### SCC tests

The specimens were cut from a plate sample of 0.30 mm thickness and a mid section was reduced in width to a cross section of 1 mm<sup>2</sup>. The total exposed area of the specimens was 1.28 cm<sup>2</sup> and the rest of the sample was masked with insulating varnish to eliminate any parasitic interactions during testing (Fig. 1). Specimens were stressed directly by loading at a specific stress level and the time to failure (TTF) of each sample was recorded. Experiments at three different stress levels (40.8, 61.2, 81.6 MPa) were carried out. During the test, the corrosive environment was renewed at a constant rate of 70 ml.h<sup>-1</sup>. A galvanostatically controlled anodic current of 5 A.m<sup>-2</sup> was impressed during the test. The threshold stress of the alloy used was 17.2 MPa. Six specimens were tested under each set of conditions.

To ensure that the SCC mechanism was the predominant factor for the failure of the specimens during the SCC tests, the following factors were included in the experimental design. The applied stresses,  $\sigma$ , were controlled in the region where SCC is expected (threshold stress = 17.2 MPa <  $\sigma$  = 40.8, 61.2, 81.6 MPa < yield point = 92.2 MPa). Anodic current densities applied to accelerate the SCC phenomenon were relatively low: 5 A.m<sup>-2</sup>. The present authors took into account the findings of earlier work on the influence of pure electrochemical dissolution during SCC tests of aluminium alloys in saline water, Karageorgos [21] where it was reported that "anodic dissolution is not the predominant factor when testing under anodic SCC conditions and the tests are carried out in the region where a true SCC mechanism is valid". Those results were obtained from TTF measurements of specimens under the same experimental conditions as in the present work, ie. specimens were at first pre-exposed under the same conditions of applied anodic current without load, and were then loaded to cause fracture.

Crack formation and propagation during SCC tests were examined in order to evaluate the SCC results and the influence of the addition of the malonic acid on them. The examination was carried out by direct microscopy on the bare or anodized specimens at various periods of exposure, from 1h to 30h, after the start of the SCC experiments, at the stress levels of 40.8 Mpa and 81.6 Mpa.

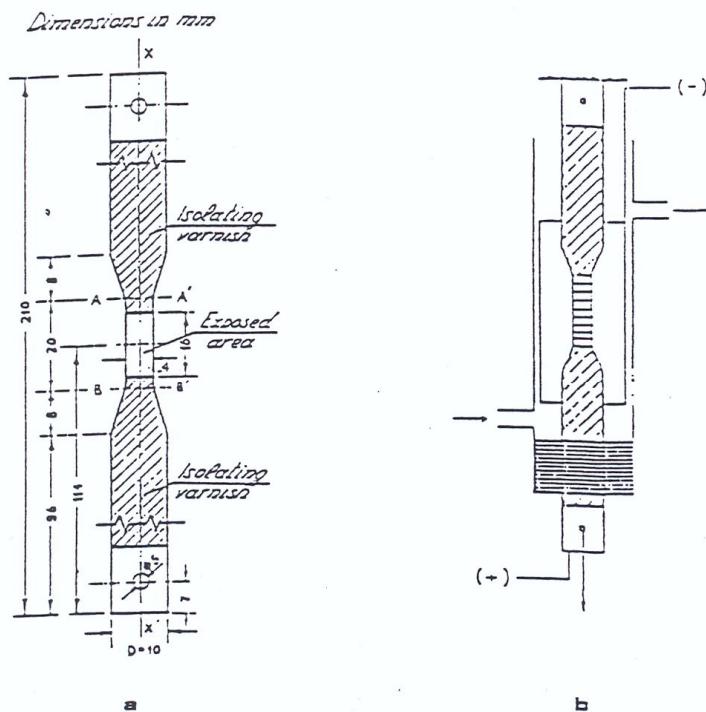


Fig.1. a) Shape and dimensions of the test specimens (AA'-BB' represents anodized area for the case of anodized specimens). b) Specimens arrangement for SCC tests.

#### Surface examination

Scanning electron microscopy (SEM) was used to study the surface of specimens after exposure. The SEM experiments were carried out with a JEOL, JSM-840 A scanning microscope, connected with a Energy Dispenser Spectrometer - EDS - (LINK, AN 10/55S).

## Results

The percentage increase in TTF of anodised as compared to bare specimens for 1050 Al-Alloy samples anodised in 3M H<sub>2</sub>SO<sub>4</sub> with an addition of various concentrations of malonic acid is shown in Fig. 2. The results show that SCC varied with concentration of malonic acid and stress level. All prepared coatings protected the bare alloy to some degree, as evident

by longer TTF. The increase in TTF was greatest in the case of 0.015 concentration of malonic acid, the protective properties being more marked at higher stress levels.

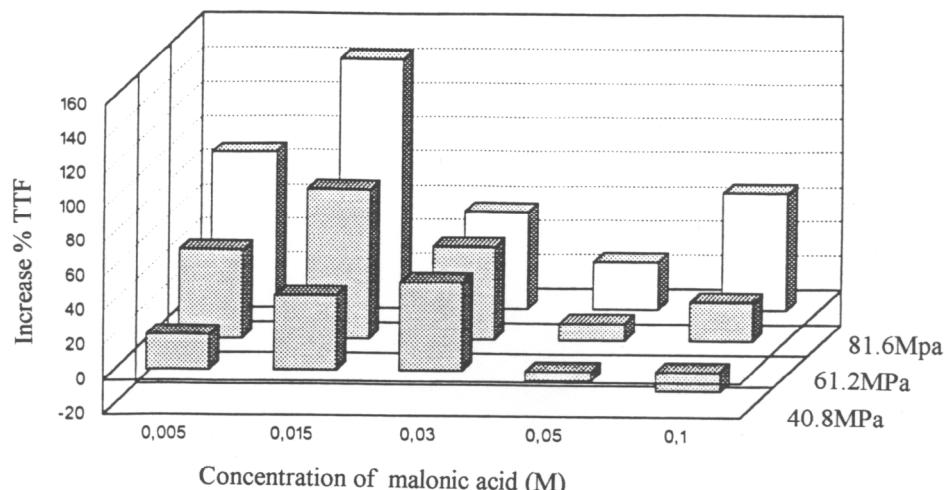


Fig.2. SCC results (% increase in TTF of anodised against bare specimen) of Al-Alloy 1050 anodised in 3M H<sub>2</sub>SO<sub>4</sub> expressed as a function of malonic acid concentration in the anodising bath.

The influence of applied potential control during SCC tests is shown in Fig. 3. From these results is evident that for the applied potentials, in the range -1.7V to +0.2V, increased times to failure were observed in the case of samples that had been anodised in solution containing malonic acid. In all cases both bare or coated specimens exhibited increased TTF when both polarised anodically and cathodically in the regions near the free corrosion potential, but TTF decreased if more anodic or cathodic was applied. TTF tended to increase in the case of malonic acid anodised sample if samples were polarised slightly more anodic than the free corrosion potential value.

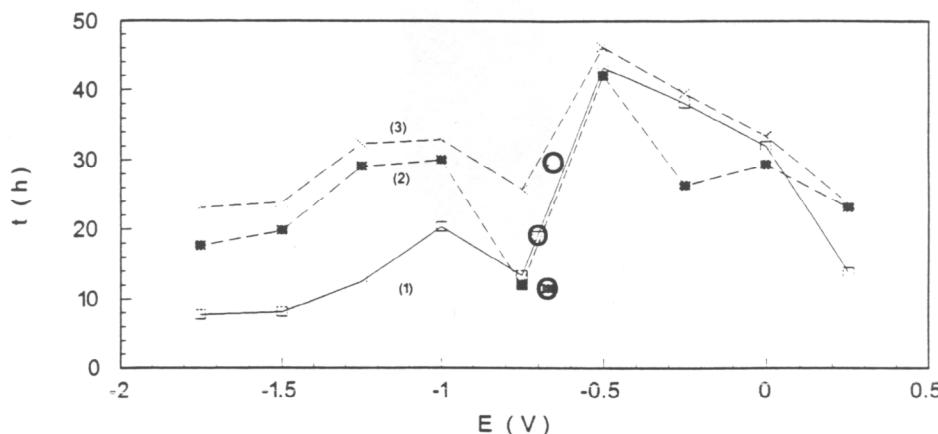


Fig.3. The influence of applied potential on time to failure for bare (1), anodised in 3M  $\text{H}_2\text{SO}_4$  (2), and anodised in 3M  $\text{H}_2\text{SO}_4 + 0.015$  malonic acid (3), Al-Alloy 1050. Free corrosion potentials also are shown (0).

## Discussion

It is reported, Spathis [20], that the addition of a 0.015M concentration of malonic acid during anodising decreased thickness and increased packing density of the coatings. This resulted in the formation of a less porous, more compact and more protective oxide layer. The results of the examination of cracks formation and propagation during SCC tests by direct microscopy observation of bare or anodized, in 3M  $\text{H}_2\text{SO}_4$  or 3M  $\text{H}_2\text{SO}_4 + 0.015$ M malonic acid, specimens at various periods of time, from 0.5h to 30h, after the start of the SCC experiments, at the stress levels of 40.8 Mpa and 81.6 Mpa, are shown in Figs. 4-9. In the case of bare specimens (Figs. 4 and 5), for both lower and higher stress levels, intensive localized corrosion phenomena were observed 0.5h after the start of the SCC experiments. After 1h it is observed abrupton of parts and formation of cracks that continued to propagate with time leading to the final decay of the metal. In the case of anodized in 3M  $\text{H}_2\text{SO}_4$  specimens (Figs. 6 and 7), localized corrosion phenomena at 0.5h after the start of the SCC experiments were also observed. After 1h of exposure, oxide layer destroy started that led to progressive increase of localized corrosion phenomena of coating and alloy, formation and propagation of cracks. In the case of anodized in 3M  $\text{H}_2\text{SO}_4 + 0.015$ M malonic acid specimens (Figs. 8 and 9), less intensive localized corrosion phenomena were observed 1h after the start of the SCC experiments, observed cracks were fewer in number and smaller in size and crack propagation was more slower than in all other cases.

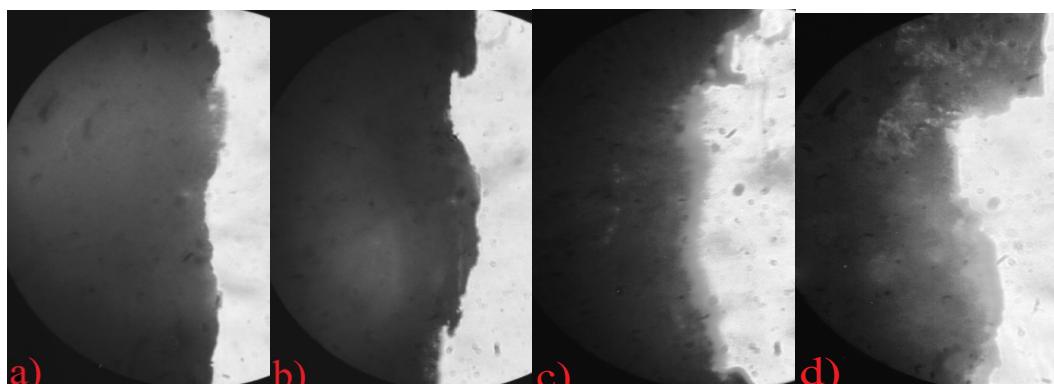


Fig.4. Post-exposure SEM micrographs of un-anodised alloy 1050 samples after various times of exposure. All samples were loaded at 81.6 Mpa, a: 0.5hr, b: 1hr, c: 3hrs, d: 5hrs, (x250).

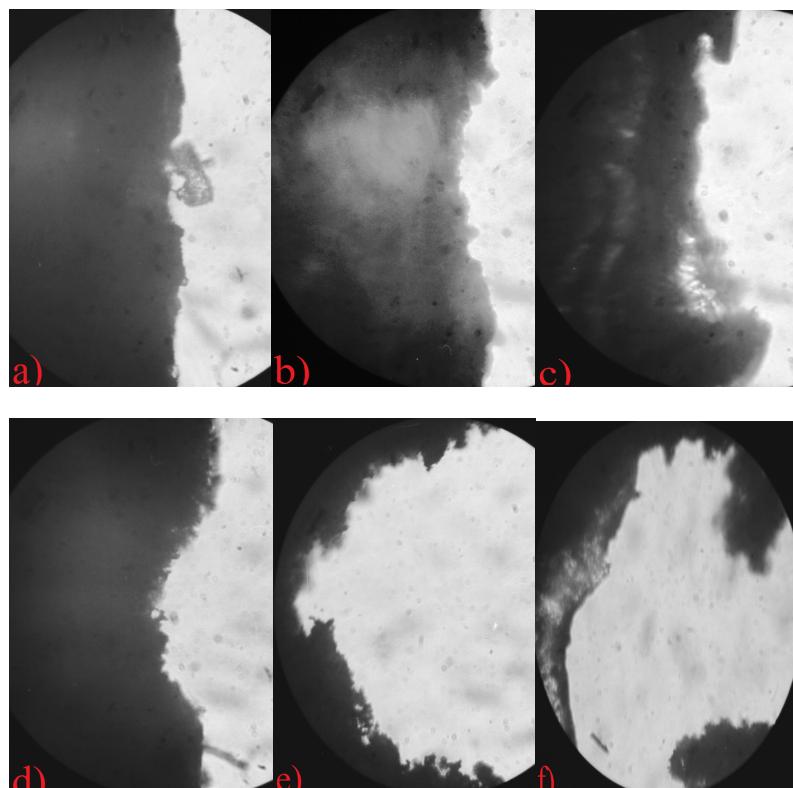


Fig.5. Post-exposure SEM micrographs of un-anodised alloy 1050 samples after various times of exposure. All samples were loaded at 40.8 Mpa, (a: 0.5hr, b: 1hr, c: 3hrs, d: 6hrs, e: 15hrs, f: 30hrs, (x250).

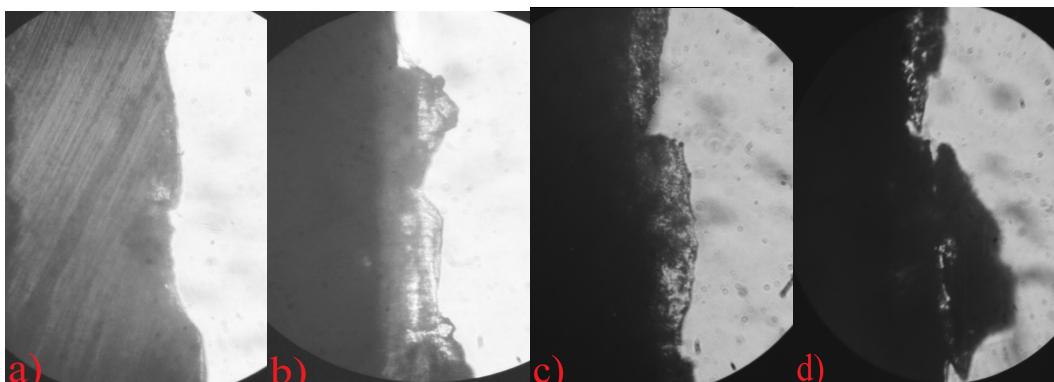


Fig.6. Post-exposure SEM micrographs of anodised in 3M  $\text{H}_2\text{SO}_4$  alloy 1050 samples after various times of exposure. All samples were loaded at 81.6 Mpa, a: 0.5hr, b: 1hr, c: 3hrs, d: 5hrs, (x250).

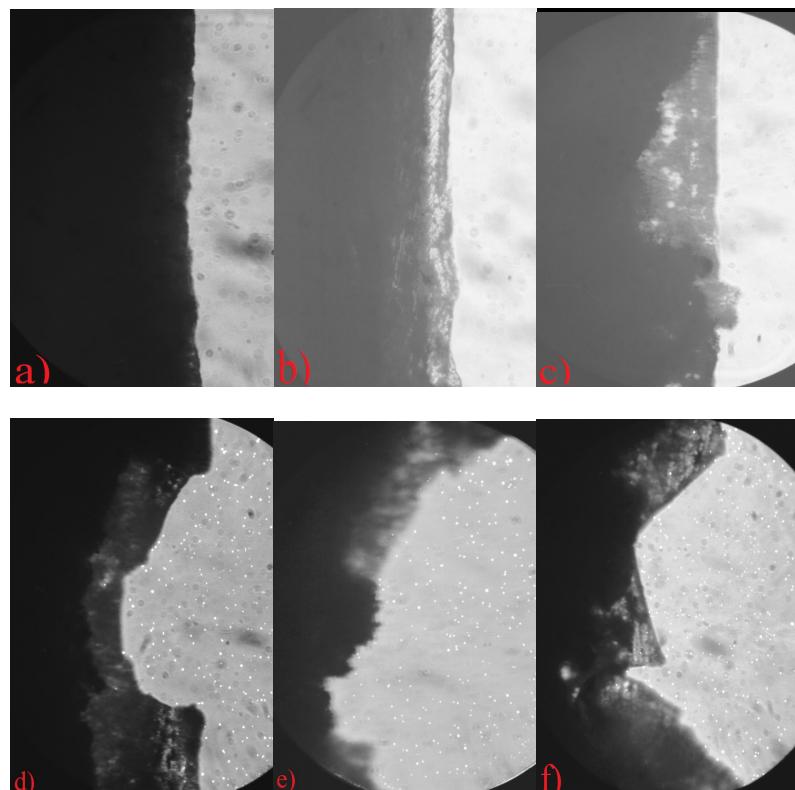


Fig.7. Post-exposure SEM micrographs of anodised in 3M  $\text{H}_2\text{SO}_4$  alloy 1050 samples after various times of exposure. All samples were loaded at 40.8 Mpa, (a: 0.5hr, b: 1hr, c: 3hrs, d: 6hrs, e: 15hrs, f: 30hrs, (x250).

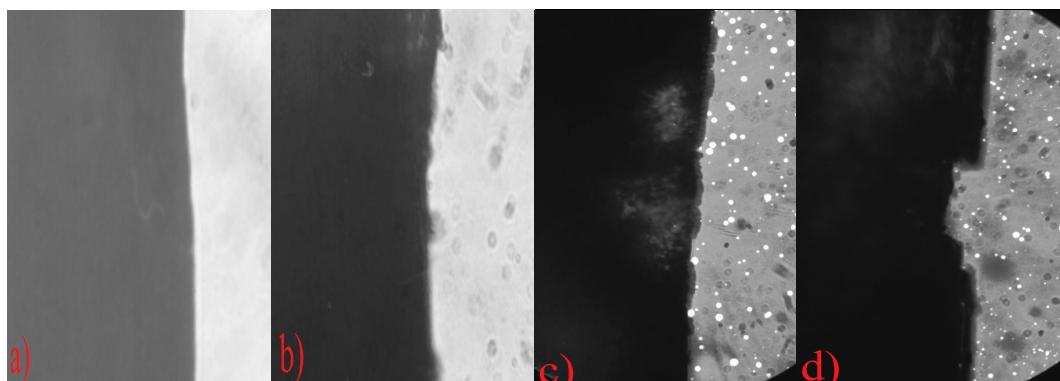


Fig.8. Post-exposure SEM micrographs of anodised in 3M  $\text{H}_2\text{SO}_4 + 0.015\text{M}$  malonic acid alloy 1050 samples after various times of exposure. All samples were loaded at 81.6 Mpa, a: 0.5hr, b: 1hr, c: 3hrs, d: 5hrs, (x250).

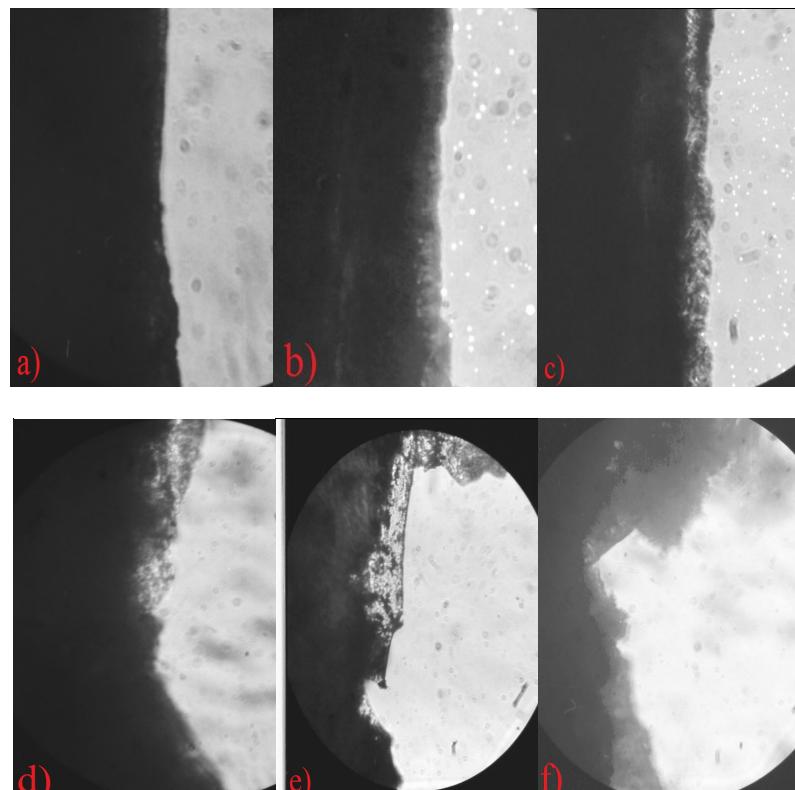


Fig.9. Post-exposure SEM micrographs of anodised in 3M  $\text{H}_2\text{SO}_4 + 0.015\text{M}$  malonic acid alloy 1050 samples after various times of exposure. All samples were loaded at 40.8 Mpa, (a: 0.5hr, b: 1hr, c: 3hrs, d: 6hrs, e: 15hrs, f: 30hrs, (x250).

The results of the examination of cracks formation and propagation, in conditions of applied potential control during SCC tests, by direct microscopy observation of bare or anodized, in 3M H<sub>2</sub>SO<sub>4</sub> or 3MH<sub>2</sub>SO<sub>4</sub> + 0.015M malonic acid, specimens at a time of 8hrs after the start of the SCC experiments, at a stress level of 61.2 Mpa, are shown in Fig.10. This examination confirmed the results of SCC tests (Fig.3). It was found that, in all cases of applied potential, specimens anodized in 3M H<sub>2</sub>SO<sub>4</sub> + 0.015M malonic acid presented less intensive localized corrosion phenomena, observed cracks were fewer in number and smaller in size and crack propagation was more slower than in the other types of specimens (bare or anodized in 3M H<sub>2</sub>SO<sub>4</sub>). Also, in all types of specimens tested, better corrosion behavior was found when a potential of -500mV was applied.

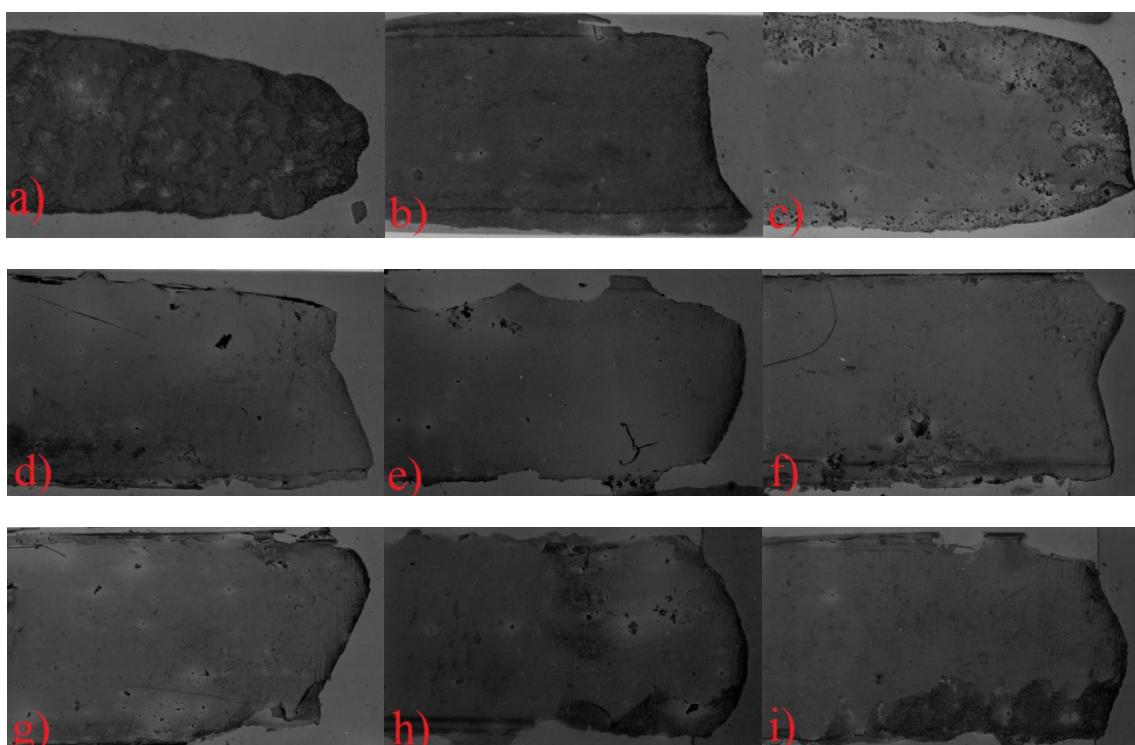


Fig.10. Post-exposure SEM micrographs of SCC specimens at  $\sigma = 61.2$  Mpa, after 8hrs of exposure and various values of applied potential: a: bare specimens at -1500mV, b: bare at -500mV, c: bare at +250mV, d: anodised in 3M H<sub>2</sub>SO<sub>4</sub> at -1500mV, e: anodised in 3M H<sub>2</sub>SO<sub>4</sub> at -500mV, f: anodised in 3M H<sub>2</sub>SO<sub>4</sub> at +250mV, g: anodised in 3M H<sub>2</sub>SO<sub>4</sub> + 0.015M malonic acid at -1500mV, h: anodised in 3M H<sub>2</sub>SO<sub>4</sub> + 0.015M malonic acid at -500mV , i: anodised in 3M H<sub>2</sub>SO<sub>4</sub> + 0.015M malonic acid at +250mV (x20).

## Conclusions

The SCC behaviour of anodised 1050 Al-Alloy was observed to vary with concentration of malonic acid, the applied anodic or cathodic polarisation during testing and especially the magnitude of the applied stress. All anodised samples protected the alloy to some degree, with better protection being observed in the case of 0.015 concentration of malonic acid.

Anodic coatings prepared in these conditions exhibited improved mechanical properties as indicated from the increased protection at a higher stress level.

Crack formation and propagation on anodized samples was slower, and observed cracks and local corrosion phenomena were fewer in number and smaller in size than in all other cases.

Prepared coatings were observed to increase corrosion resistance where externally applied potentials were slightly more anodic than the free corrosion potential values. Reverse effect was been marked with larger potentials (both anodic or cathodic) away from the free corrosion potential.

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