

Effect of Inorganic Additives on the Protection of Anodic Coated Al-Alloys against Corrosion and SCC

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Abstract

In the present work the effect of addition of some inorganic additives on stress corrosion cracking and corrosion behaviour of anodised 1050 Al-Alloy was investigated by SCC tests and electrochemical measurements. The anodic coatings were prepared electrolytically in a bath of 3M or 4M H₂SO₄ with an addition of 0.015M boric acid, sulphate nickel or borax. The SCC behaviour was found to vary with anodising conditions and stress level. Anodic coating prepared in 3M H₂SO₄ without any additives, did not protect the bare alloy, decreasing the time to failure (TTF), whereas in 4M slightly increases TTF. Addition of any of the inorganic additives used, increased the TTF with a maximum of increase in the case of sulphate nickel in 4M H₂SO₄ and at a high stress level, but the general behaviour for all stress levels, as also in without stress corrosion conditions, is better in the case of addition of 0.015M borax in 3M H₂SO₄. For the interpretation of the results, SEM micrographs and the chemical compositions of the surfaces of the stress corrosion tested specimens were obtained. Properties of the anodic coatings as thickness, packing density, coating ratio, roughness, were also studied. The anodic coatings formed in a electrolytic bath with additives present were found to be less porous, and more compact, having better anticorrosive and mechanical properties.

Keywords: SCC, Protection, Aluminium, Anodic Coatings, Boric Acid, Sulphate Nickel, Borax.

Introduction

The SCC behaviour of Al-alloys of the 1XXX series is rarely studied because the high strength Al-alloys, eg. 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], Dolic [4], Dollah [5].

Some Al-alloys used in practice, are anodically oxidised, for protection against corrosion and SCC. It has been shown that during anodising, a porous Al_2O_3 film with a cellular structure up to a thickness of 36 μm 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, [6], Skoulikidis, [7], Skoulikidis, [8], Mert [9].

Many studies, Lyberatos [10], Monticell [11], Popovic [12], Ozyilmaz [13], Breslin [14], Galkowski [15], Trabelsi [16], Grandfield [17], Chattopadhyay [18], 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, Lazbourn [19], Kouloumbi [20], Patil [21], Yu [22], Souza [23].

The aim of this work is the study of the effect of addition of some inorganic compounds on corrosion and stress corrosion cracking behaviour of anodised 1050 Al-Alloy. The investigation was carried out by SCC tests and electrochemical measurements.

Experimental

The Al-Alloy tested was pure aluminium ($\text{Al} > 99.5\%$), ASTM 1050, H38 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 or 4M H_2SO_4 with an addition of 0.015M boric acid (H_3BO_3), sulphate nickel ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$) or borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), at a current density of 6 $\text{A} \cdot \text{dm}^{-2}$, at 25°C and their thickness was

estimated [7] to 10 μm . The real thickness of the coatings was confirmed by direct microscopy examination of the cross sections of 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 mm². The total exposed area of the specimens was 1.28 cm² 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⁻¹. A galvanostatically controlled anodic current of 5 A.m⁻² 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, σ , were controlled in the region where SCC is expected (threshold stress = 17.2 MPa < σ = 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⁻². 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 [24] 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.

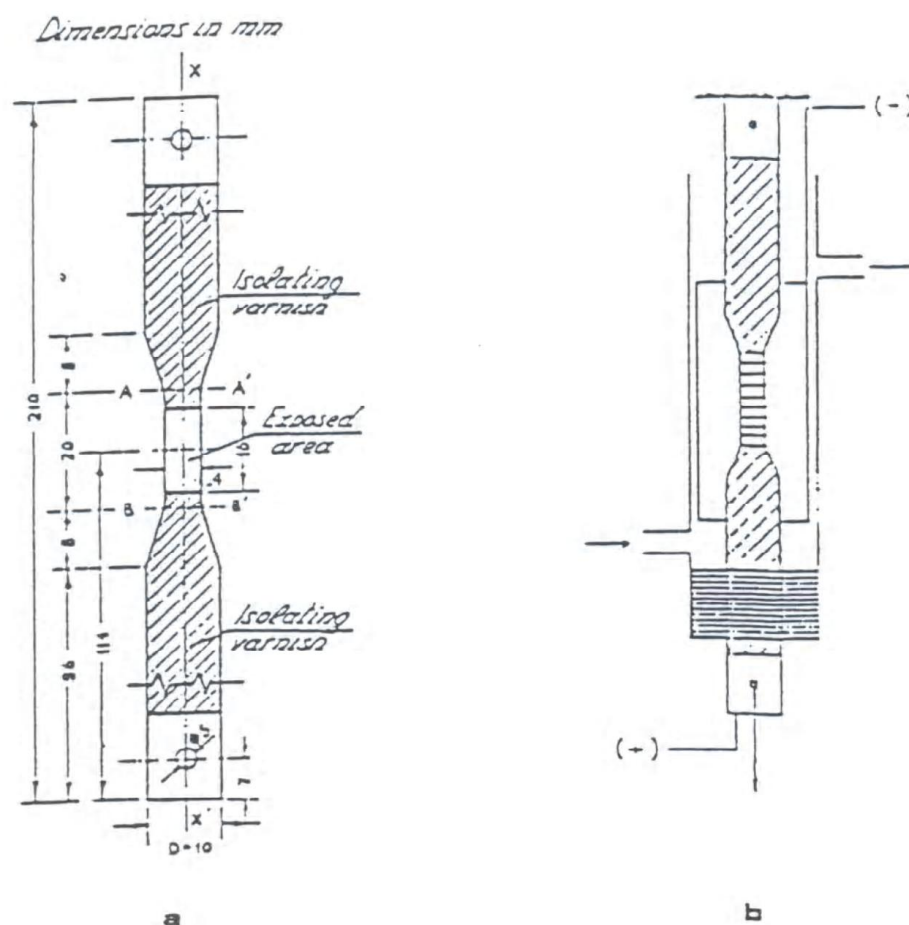


Fig.1a) Shape and dimensions of the test specimens (AA'-BB' represents anodized area for the case of anodized specimens). b) Specimens arrangement for SCC tests.

Polarization tests

The specimens were also cut from a plate of the same thickness (0.30 mm), the dimensions were 1 cm x 5 cm and the total exposed area was 2 cm² (the rest was also masked with insulating varnish).

The cyclic anodic potentiodynamic polarization measurements were carried out with standard methods, ASTM [25], ASTM [26], ASTM [27], without any agitation or renewal of the solution, at a slow scan rate of 0.6 V/h. Before starting the potential scan, the specimens were immersed in the test solution for 1 h to reach a steady state of equilibrium (open circuit corrosion potential, E_{cor}). A potentiostat-galvanostat (Bank PGS-81) with a scan generator (Bank VSG-72) and a X-Y recorder, platinum counter electrode and saturated calomel reference electrode (SCE) were used.

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).

Packing Density

For the calculation of the packing density, the weight of the anodic coating, its thickness and the oxidised area of the specimen were measured. The packing density was calculated as the ratio of weight to volume of each anodic coating.

Coating Ratio

The coating ratio, i.e., the coulombic efficiency for the formation of porous oxide films on Al, was calculated by the ratio of the weight of oxide formed to the weight of aluminium consumed.

Roughness

The roughness of surface of the anodic coatings was measured with a perthometer (PERTHEN C 5D with a tracer drive unit PVK) and the roughness factor that was used in our experiments was the mean arithmetic value of all the distances of the roughness diagram from its central line.

Results and Discussion

In Fig. 2 SCC results (increase % of TTF of anodised against bare specimens) of anodised in 3M or 4M H₂SO₄ 1050 Al-Alloy and with an addition of 0.015M of various inorganic additives are shown. The SCC behaviour was found, from these results, to vary with anodising conditions and stress level. Anodic coating prepared in 3M H₂SO₄ without any additives, did not protect the bare alloy, decreasing the time to failure (TTF), whereas in 4M slightly increases TTF. Addition of any of the inorganic additives used, increased the TTF with a maximum of increase in the case of sulphate nickel in 4M H₂SO₄ and at a high stress level, but the general behaviour for all stress levels is better in the case of addition of 0.015M borax in 3M H₂SO₄.

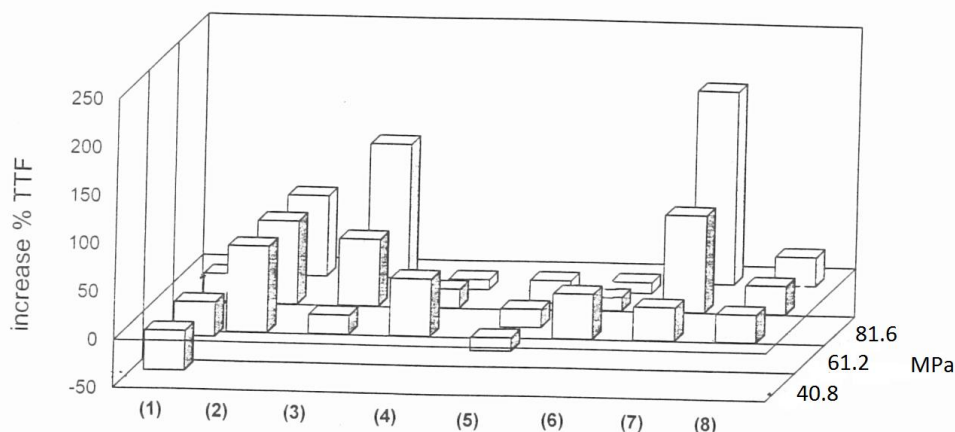


Fig.2 SCC results (increase % of TTF of anodised against bare specimens) of anodised in 3M or 4M H_2SO_4 1050 Al-Alloy and with an addition of 0.015 M of various inorganic additives: (1): 3M H_2SO_4 , (2): 3M H_2SO_4 + borax, (3): 3M H_2SO_4 + sulphate nickel, (4): 3M H_2SO_4 + boric acid, (5): 4M H_2SO_4 , (6): 4M H_2SO_4 + borax, (7): 4M H_2SO_4 + sulphate nickel, (8): 4M H_2SO_4 + boric acid.

In Figures 3 and 4 the potentiodynamic polarization curves of bare or anodised 1050 Al-Alloy in 3M and 4M H_2SO_4 correspondingly and with an addition of 0.015M of various inorganic additives are shown. From these results it follows that in all cases the Al-Alloy suffers localized corrosion. This is indicated from the presence of Epit in a more positive value than E_{COR} and also from the presence of a hysteresis loop between the forward and reverse scan currents, Baboian [28]. In all cases the Al-Alloy is not passivated, as passive regions do not appear for potential values more positive than Epit and reverse currents are always higher than forward currents. It is also observed that the addition of inorganic additives did not significantly influence E_{COR} but shifted Epit in the noble direction (-640 mV for 0.015M borax in 3M H_2SO_4) relative to the bare alloy (-680 mV) and decreased anodic currents indicating less susceptibility to localized corrosion in the free corrosion potential regions. In the absence of any additive, Epit shifted in the active direction (-720 mV for 3M H_2SO_4).

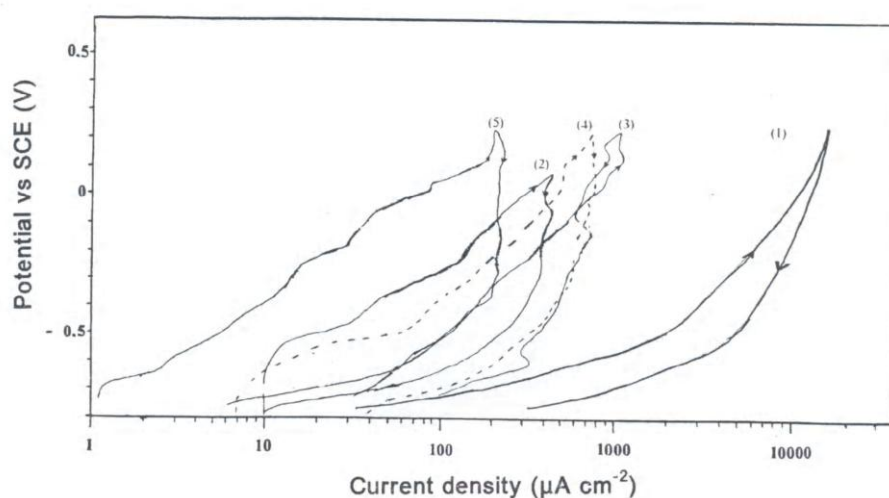


Fig.3 Potentiodynamic polarization curves of bare or anodised in 3M H₂SO₄ 1050 Al-Alloy for various additions of 0.015 M of various inorganic additives: (1): bare Al, (2): 3M H₂SO₄, (3): 3M H₂SO₄ + sulphate nickel, (4): 3M H₂SO₄+ boric acid, (5): 3M H₂SO₄ + borax.

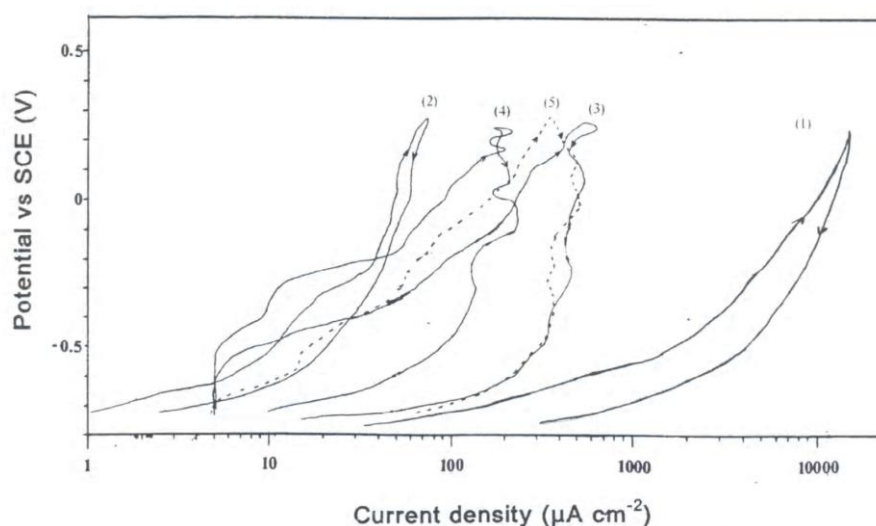


Fig.4 Potentiodynamic polarization curves of bare or anodised in 4M H₂SO₄ 1050 Al-Alloy for various additions of 0.015 M of various inorganic additives: (1): bare Al, (2): 4M H₂SO₄, (3): 4M H₂SO₄ + sulphate nickel, (4): 4M H₂SO₄+ boric acid, (5): 4M H₂SO₄ + borax.

From the results of Figures 5,6, follow that increase of the TTF is correlated with a smaller amount of Cl⁻ present on the fracture surface of tested specimens (with a minimum value of 0.11% for borax and a maximum of 0.30% for 3M H₂SO₄ without additives). Also that

during SCC, anodic coating is destroyed and new oxide layers are formed, resulting in a decrease of sulphur content and an increase of oxygen content, as indicated from the decreased content in sulphur and increased in oxygen in the side surface of the stress corrosion tested specimens than in the corresponding non-tested specimens (Fig. 6) Both corrosion and especially stress resistance of the coating are better when prepared in presence of borax as shown from the SEM micrographs of SCC tested specimens (Fig. 7).

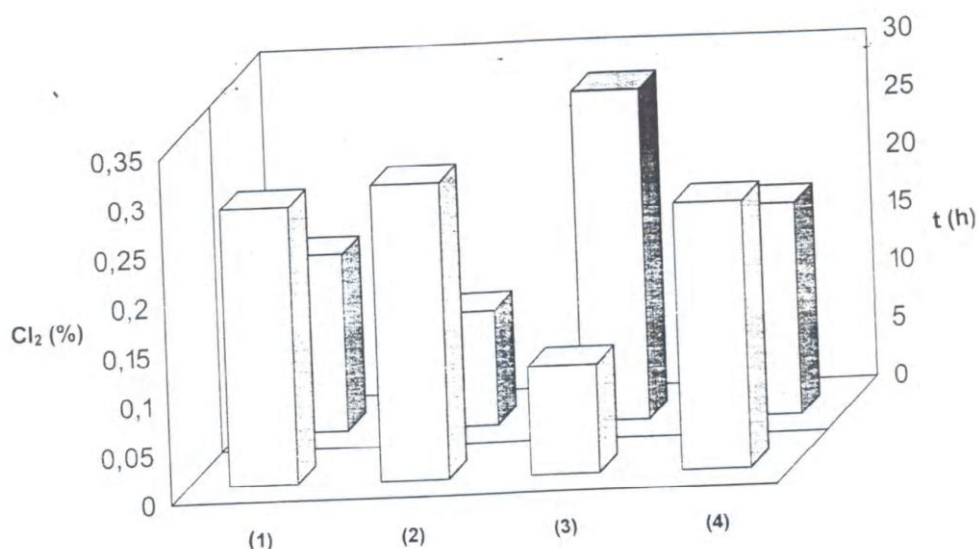


Fig.5 Chloride content in fracture surface of stress corrosion tested specimens and corresponding times to failure of bare (1), anodised in 3M H_2SO_4 (2), 3M H_2SO_4 + borax (3), 3M H_2SO_4 + boric acid (4).

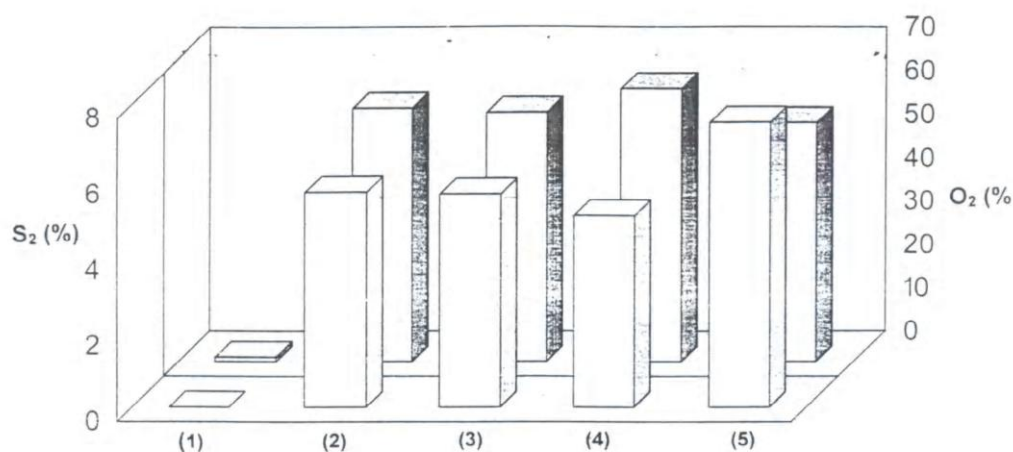


Fig.6 Sulphur and oxygen content in side surface of stress corrosion tested specimens of bare (1), anodised in 3M H₂SO₄ (2), 3M H₂SO₄ + borax (3), 3M H₂SO₄+ boric acid (4), anodised and non-tested (5).

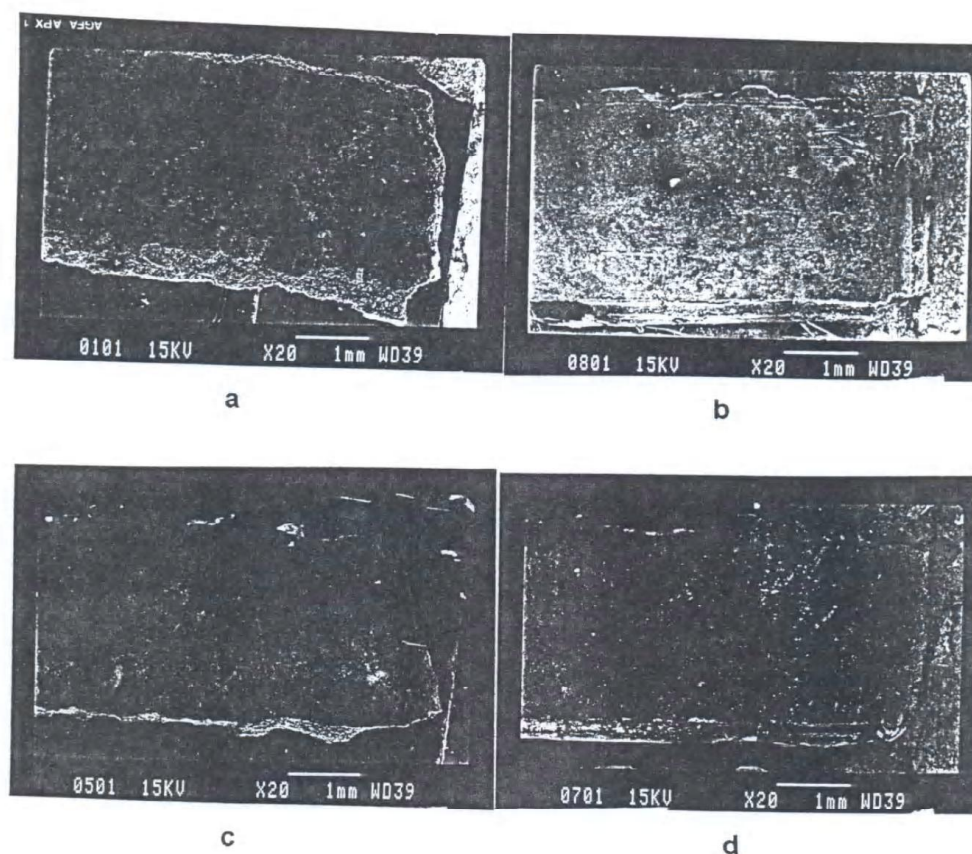


Fig.7 SEM micrographs of SCC tested specimens at $\sigma = 6.25 \text{ kg/mm}^2$

a: bare specimens, b: anodised in 3M H₂SO₄, c: anodised in 3M H₂SO₄ + 0.015M borax, d: anodised in 3M H₂SO₄ + 0.015M boric acid.

The measurements of some physical properties of the anodic coatings shown in Table 1 indicate that the addition of inorganic additives during anodising decreases thickness and increases packing density of the coatings resulting in the formation of a less porous oxide layer. The coating ratio increases in the presence of additives, while roughness decreases. These results can be explained from the lower presence of sulphur in the oxide film (6.68% in presence of borax and 7.36% without any addition), due to lower incorporation of anions into the oxide structure during anodising in presence of the additives and also from the possible absorption of these compounds on the metal surface or the formation of some complexes on it. Further investigation is necessary to confirm this assumption.

Table 1

Some physical properties of anodic coating prepared in 3M H₂SO₄ in presence or not of additives

Anodising conditions	oxide thickness (μm)	packing density (gr/cm ³)	coating ratio	roughness (μm)
3M H ₂ SO ₄	11.86	2.56	1.42	0.258
3M H ₂ SO ₄ + 0.015M borax	10.28	2.90	1.44	0.242
3M H ₂ SO ₄ + 0.015M boric acid	11.68	2.65	1.43	0.254

Conclusions

1. The SCC behaviour of anodised 1050 Al-Alloy was found to vary with anodising conditions and stress level. Anodic coatings prepared in 3M or 4M H₂SO₄ without any additives, did not protect the bare alloy. Addition to the anodising solution of any of the inorganic additives used, had as result a protection of the alloy, with better protective properties in the case of borax.

2. The addition of inorganic additives during anodising decreases thickness and roughness and increases packing density and coating ratio of the coatings, resulting in the formation of a less porous and more compact oxide layer.

3. An explanation of the mechanism of the effect of inorganic additives on oxidation and SCC behaviour of Al-Alloys is the absorption of these compounds on the metal surface or the formation of some complexes on it.

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