Corrosion inhibition of pure aluminium and AA2014-T6 alloy by strontium chromate at low concentration

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The influence of a low concentration of strontium chromate on the corrosion inhibition of superpure aluminium and AA2014-T6 aluminium alloy in 0.6 M chloride solution has been investigated to simulate the leaching process of inhibitors from coatings. The potential-time and polarisation behaviour show influences on both the anodic and cathodic kinetics on the superpure aluminium surface. However, predominant cathodic inhibition was observed for the AA2014-T6 aluminium alloy. It was evident that chromium species were reduced at cathodic second phase particles, forming a thin passive film at the cathodic sites, which blocks the oxygen reduction reaction and, consequently, provides effective corrosion inhibition. Copyright © 2015 The Authors Surface and Interface Analysis Published by John Wiley & Sons Ltd.

Keywords: corrosion inhibition; chromate; pure aluminium; aluminium alloy

Introduction

Chromate-containing pigment is employed in aerospace primer coatings due to the superior corrosion protection provided to aluminium and its alloys.1–4 One of the functions of a chromate-containing primer is to inhibit corrosion by release of chromate ions when the paint system is damaged, e.g. at cracks, scratches, crevices or cut edges. The chromate ions leach from the primer and migrate to the damaged area to passivate the exposed metal.5–8 In galvanic coupling tests of chromate inhibition on an aluminium/copper couple or an AA2024/AA2024 aluminium alloy couple, the former coupling revealed a significant reduction of the cathodic current on copper but little effect on aluminium. The latter coupling led a decreased current in both the net anode and the net cathode compartments. The results imply that chromate cathodically inhibits oxygen reduction on copper or copper-containing particles,9 but may also provide anodic inhibition with the alloy. This view is also supported by Kendig et al.10 Further, during salt spray exposure of AA2024 aluminium alloy coated with chromate-containing pigment, chromate species have been detected on damaged areas of the alloy, particularly on second phase particles, smears formed by the milling process and pits.5–8 It has also been suggested that chromate blocks the pores or defects in the coating.11 The pigment solubility significantly influences the overall performance.12 Low solubility strontium chromate and barium chromate perform better than the more soluble sodium chromate and calcium chromate.12 The presence of chromium (VI) species in pretreatment layers, such as chromate conversion coating,13,14 or anodic films,15 applied before the primer is also important, as the species are also able to protect the metal if the coating is damaged.13–17

In view of the role of chromate species in pretreatment layers and primer coatings, it is important to understand the influence of low concentrations of chromate on the effectiveness of corrosion inhibition. In the present work, the effects of a relatively low concentration of strontium chromate (3.3 × 10−5 M) on the electrochemical behaviour of superpure aluminium, i.e. containing little second phase, and AA2014-T6 alloy, i.e. an alloyed material of high corrosion susceptibility, have been studied by open circuit potential, anodic and cathodic polarisation. Further, transmission electron microscopy was employed for a direct observation of the corrosion of AA2014 aluminium alloy in chloride solution and the protection of the alloy in a chloride solution containing a low concentration of chromate.

Experimental

Superpure aluminium (99.99 wt%, with impurities of 0.002 wt% copper, 0.003 wt% silicon and 0.004 wt% iron) was provided as rolled sheet of 0.6-mm thickness. Rolled AA2014-T6 aluminium alloy of 1-mm thickness was also used for the study. The composition of the alloy is 0.5–1.2 Si, 0.7 Fe, 3.9–5.0 Cu, 0.4–1.2 Mn, 0.2–0.8 Mg, 0.10 Cr, 0.25 Zn, 0.15 Ti (wt%) and Al bal.

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The superpure aluminium was electropolished in 20% (v/v) perchloric acid (60 wt%) and 80% (v/v) ethanol at 20 V for 5 min below 10 °C. After electropolishing, the specimens were rinsed thoroughly in deionised water and dried in a cool air stream. Because electropolishing in acid solution removes second phase particles, the AA2014-T6 aluminium alloy was etched in 3 g/l sodium hydroxide solution for 8 min at 25 °C, rinsed with water, then desmutted in 50% (wt) nitric acid for 30 s at 25 °C, rinsed with water and finally dried in a cool air. The specimens were then masked with beeswax and colophony (1:3 wt/wt) to leave an exposed surface area of 1 × 1 cm² and stored in a desiccator over silica gel.

Open circuit potential-time response and polarisation studies were performed in naturally aerated 0.6 M sodium chloride (NaCl) solution alone, or with 3.3 × 10⁻⁶ M added strontium chromate. Polarisation was performed using a three-electrode cell, with a platinum sheet counter electrode and a saturated calomel electrode connected by a Luggin probe. Before polarisation, each specimen was immersed in the selected electrolyte for 30 min to allow the potential to reach a steady value. Separate specimens were polarised in the cathodic or anodic direction at a scan rate of 7.5 mV/min. Cathodic polarisation was carried out from the open circuit potential to a potential 0.3 V below the open circuit potential. Anodic polarisation was commenced from 0.01 V below the open circuit potential to potentials above the pitting potential. The potential and polarisation behaviour were recorded using a Schlumberger 1280 potentiostat (Solartron Analytical, Farnborough, UK).

The AA2014-T6 aluminium alloy was ultramicrotomed with a diamond knife to generate sections with a nominal thickness of 15 nm. The sections were immersed in 0.6 M NaCl solution, without and with 3.3 × 10⁻⁶ M strontium chromate. The sections were then rinsed by deionised water and dried with a filter paper before examination by transmission electron microscopy (TEM), with associated energy dispersive X-ray (EDX) analysis.

**Results and discussion**

**Potential-time and polarisation behaviour**

The potential-time responses of the superpure aluminium and AA2014-T6 aluminium alloy in 0.6 M NaCl, with and without chromate are shown in Fig. 1. For superpure aluminium, the trend of potentials in the absence or presence of chromate species were very similar, but an increase of the potential from −1.129 to −1.000 V was observed after 30 min when the superpure aluminium was immersed in chloride solution with chromate. In contrast, the potential of AA2014-T6 aluminium alloy remained in the range −0.70 to −0.72 V for both electrolytes (Fig. 1b).

The anodic polarisation behaviours of the superpure aluminium and the AA2014-T6 aluminium alloy are shown in Fig. 2. Polarisation of the superpure aluminium without chromate resulted in an initial region of passivity, followed by pitting corrosion, which led to a steeply increasing current density (Fig. 2a). A similar behaviour was evident in the presence of added chromate, although the passive current density, estimated at a potential midway between the open-circuit and pitting potentials, was reduced from the order of 10⁻⁷ A/cm² to the order of 10⁻⁸ A/cm². However, the pitting potentials of −0.745 V and −0.749 V without and with chromate addition differed negligibly (Fig. 2a). The anodic polarisation...
behaviours of AA2014-T6 alloy in the chloride solutions in the presence or absence of $3.3 \times 10^{-6}$ M chromate are similar (Fig. 2b) with no passivation regions evident (Fig. 2b).

The cathodic polarisation behaviours of the superpure aluminium and the AA2014-T6 aluminium alloy in 0.6 M NaCl, in the presence and absence of strontium chromate, are shown in Fig. 3. The current density during cathodic polarisation of pure aluminium progressively increased, suggesting both oxygen reduction and hydrogen evolution may be contributing to the cathodic reaction at different potentials (Fig. 3a). When chromate was present, the cathodic polarisation curve shifted to lower current densities, indicating a reduction of the rate of the cathodic reactions (Fig. 3a). For AA2014-T6 aluminium alloy, the cathodic polarisation behaviour in chloride only solution revealed a diffusion controlled process upon polarisation, with a limiting current density, due to the oxygen reduction reaction, of about $1.3 \times 10^{-5}$ A/cm$^2$, measured at a potential midway between the open-circuit potential and the final potential (Fig. 3b). Addition of chromate changed the shape of the cathodic polarisation curve of the AA2014-T6 aluminium alloy accompanied by a significant reduction of the current density, which revealed a strong cathodic inhibition (Fig. 3b). The behaviour is further discussed in Section 4.

Transmission electron microscopy observation and energy dispersive X-ray analysis

Thin ultramicrotomed alloy sections were used to investigate the corrosion behaviour of the alloy in NaCl solution and the effect of a low concentration of chromate on the behaviour. Immersion of the ultramicrotomed alloy sections in chloride solution resulted in significant alkaline corrosion at the periphery of AlFeMnCuSi (Fig. 4a) and CuAl$_2$ second phase particles, which are major constituent phases of the alloy, because of the oxygen reduction reaction. Pitting corrosion and corrosion at the grain boundaries were also evident. In the presence of $3.3 \times 10^{-6}$ M chromate, alkaline corrosion adjacent to the particles was prevented (Fig. 4b). EDX analysis showed the presence of chromium species on the AlFeMnCuSi particle (Fig. 5a). Further, hardly any chromium is detected at the adjacent alloy matrix (Fig. 5b). Strontium species were not detected on the particles or the alloy matrix, suggesting that it is chromium species, and not strontium species, which inhibited corrosion at such low concentration.

Discussion

Influence of chromate on superpure aluminium

The open circuit potential and anodic polarisation behaviour reveal that superpure aluminium in 0.6 M chloride solution is in the passive state under natural immersion conditions, with a potential around
Influence of chromate on AA2014-T6 aluminium alloy

Combining the observation of the open circuit potential and anodic polarisation, it is considered that the alloy in 0.6 M chloride solution is in the pitting potential region during natural immersion. A rapid increase in anodic current density was evident upon anodic polarisation. In contrast to the superpure aluminium, the addition of chromate species had negligible influence on the open circuit potential, the pitting potential or anodic current density for the alloy, suggesting that little anodic inhibition was achieved by the low chromate concentration. On the cathodic side, addition of chromate changed the shape of the cathodic polarisation curve, accompanied by a significant reduction of the cathodic current density, as shown in Fig. 3b, suggesting a significant cathodic inhibition from 3.3 × 10^{-6} M strontium chromate. Comparing the cathodic polarisation behaviour with the anodic polarisation behaviour, it is evident that the corrosion is under the control of the cathodic activity, and the reduction of the cathodic current density should result in a reduction of the corrosion rate.

From the electrochemical behaviour and microscopic observation, it is evident that the strontium chromate is a cathodic inhibitor at the low concentration of 3.3 × 10^{-6} M for AA2014-T6 aluminium alloy. Further, a reduction of the concentration of strontium chromate to 3.3 × 10^{-7} M greatly weakened this cathodic inhibition, suggesting that the order of 10^{-6} M is a critical concentration for effective cathodic inhibition by strontium chromate for the AA2014-T6 aluminium alloy. Interestingly, sodium chromate at a low concentration of 10^{-5} M showed a similar behaviour to strontium chromate, suggesting that the findings of the present study are applicable to other types of chromate.

Chromium species may form a thin passive film by reduction from chromium (VI) species to chromium (III) species at cathodic sites, which block the oxygen reduction reaction and, consequently, prevent corrosion.

Conclusions

1. Strontium chromate showed both anodic and cathodic inhibition at a low concentration of 3.3 × 10^{-6} M for superpure aluminium when immersed in 0.6 M NaCl solution.

2. Strontium chromate at the low concentration of 3.3 × 10^{-6} M is mainly a cathodic inhibitor for the AA2014 aluminium alloy in 0.6 M NaCl solution, with little influence on the anodic kinetics because the alloy is in the pitting potential region during natural immersion in the solution. Its cathodic inhibition was revealed by the significant reduction of cathodic current density during cathodic polarisation and the formation of a thin film observed on cathodic second phase particles.

3. At the low concentration investigated, chromate has no effect on the pitting potential for both superpure aluminium and AA2014-T6 aluminium alloy.

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References

[1] A. E. Hughes, A. Trinchi, F. F. Chen, Y. S. Yang, I. S. Cole, S. Sellaiyan, J. Carr, P. D. Lee, G. E. Thompson, T. Q. Xiao, Adv. Mater., 2014, 26, 4504.

[2] A. E. Hughes, A. Trinchi, F. F. Chen, Y. S. Yang, I. S. Cole, S. Sellaiyan, J. Carr, P. D. Lee, G. E. Thompson, T. Q. Xiao, Prog. Org. Coat., 2014, 77, 1946.

[3] A. E. Hughes, S. Mayo, Prog. Org. Coat., 2012, 74, 726.

[4] A. Trueman, S. Knight, J. Colwell, T. Hashimoto, J. Carr, P. Skeldon, G. E. Thompson, Corros. Sci., 2013, 75, 376.

[5] S. A. Furman, F. H. Scholes, A. E. Hughes, D. N. Jamieson, C. M. Macrae, A. M. Glenn, Corros. Sci., 2006, 48, 1827.

[6] S. A. Furman, F. H. Scholes, A. E. Hughes, D. Lau, Prog. Org. Coat., 2006, 56, 33.

[7] F. H. Scholes, S. A. Furman, A. E. Hughes, T. A. Markley, Corros. Sci., 2006, 48, 1812.

[8] F. H. Scholes, S. A. Furman, A. E. Hughes, T. Nikpour, N. Wright, P. R. Curtis, C. M. Macrae, S. Intern, A. J. Hill, Prog. Org. Coat., 2006, 56, 23.

[9] W. J. Clark, J. D. Ramsey, R. L. McCreery, G. S. Frankel, J. Electrochem. Soc., 2002, 149, B179.
[10] M. Kendig, S. Jeanjaquet, R. Addison, J. Waldrop, Surf. Coat. Technol. 2001, 140, 58.
[11] P. Carbonini, T. Monetta, L. Nicodemo, P. Mastronardi, B. Scatteia, F. Bellucci, Prog. Org. Coat. 1996, 29, 13.
[12] J. Sinko, Prog. Org. Coat. 2001, 42, 267.
[13] L. Xia, E. Akiyama, G. Frankel, R. McCreerya, J. Electrochem. Soc. 2000, 147, 2556.
[14] V. Laget, C. S. Jeffcoate, H. S. Isaacs, R. G. Buchheit, J. Electrochem. Soc. 2003, 150, B425.
[15] S. J. Garcia-Vergara, P. Skeldon, G. E. Thompson, H. Habazaki, Surf. Interface Anal. 2007, 39, 860.
[16] R. G. Buchheit, A. E. Hughes, ASM Handbook, Volume 13A: Corrosion: Fundamentals, Testing, and Protection, (Eds: S. D. Cramer, B. S. Covino Jr), Ohio (USA), 2003, pp. 720–735.
[17] M. W. Kendig, R. G. Buchheit, Corrosion 2003, 59, 379.
[18] Y. Liu, Protection of aluminium alloy by chromate species, PhD thesis, The University of Manchester Institute of Science and Technology (UMIST), Manchester (UK), November 2001.
[19] Y. Liu, G. E. Thompson, P. Skeldon, C. J. E. Smith, K. Shimizu, Y. Kihn, Proceedings of 2nd International Symposium on Aluminium Surface Science and Technology, Manchester, England, 2000; p473.