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Corrosion protection of AA6061 T6-10% Al_2O_3 composite by molybdate conversion coatings

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Abstract

The corrosion protection performance of aluminum composite materials was investigated in 3.5% NaCl solution for time ranging between 1–60 days. Series of specimens were treated in molybdate solutions under different conditions. Free immersion and electrochemical activation techniques were used to apply the molybdate layer. The specimens which were directly treated or pickled before molybdate treatment showed severe pitting corrosion. Conversely, the specimens which were subjected to an oxide thickening step before the molybdate treatment showed outstanding corrosion protection. XPS revealed a higher amount of molybdate as MoO_4^{2-} for the specimens prepared by electrochemical activation technique than for the free immersion technique.

1. Introduction

Molybdate is the most versatile inhibitor largely mimicking chromate in the variety of applications served. The first practical use of molybdate for corrosion inhibition was in automotive engine coolants [1].

When environmental laws restricted chromate use in cooling tower waters, molybdate–zinc treatments began to be used as the replacement. Molybdate treatments are common and enjoy many advantages. Besides its environmental acceptability, molybdate gives multimetal protection, is effective in salt solutions, and is both thermally and chemically stable [1].

The interaction of molybdates with Al and their impact on the corrosion resistance of Al have been the subject of several papers [2–8]. Wiggle et al. [2] studied the effect of molybdates on the pitting behavior of two aluminum alloys, AA3003 and AA7072, in ethylene glycol/water/molybdate mixtures and found that E_b becomes more noble, increasing monotonically with the concentration of molybdate anions in the solution. Stranick [3] found that molybdates increase E_b for AA 300 in hard water containing 250 ppm Cl^- under neutral and alkaline conditions. Stranick [3] and El-Sobki et al. [4] found that the molybdate anions decrease the general corrosion as well as the pitting behavior of aluminum. Increasing the molybdates concentration from 100 to 2000 mg L^{-1} resulted in an electropositive shift of E_{oc} for AA 3003 [3]. The loss in weight of pure Al measured by El-Sobki et al. in neutral and alkaline saline solution showed that increasing the molybdate concentration resulted in lower corrosion rates and more noble values for E_{oc} [4].

Investigations of the influence of the molybdate anion on the chemistry of the passive film at both E_{oc} and more electropositive potentials have shown that molybdenum is incorporated into the film and is reduced to a Mo^{4+} state. However, the detailed description of the passive film and its interaction with the molybdate solution varies from study to study. In their studies of the effect of molybdates on the film growth of pure Al in boiling water, McCune et al. [5] found significant oxidation and film growth on the surface. The films consisted primarily of an unidentified Mo precipitate and contained very little Al. XPS studies on the effect of the molybdate anion in the passive film showed the presence of both Mo^{4+} and Mo^{6+} [3, 6, 7].

Augustynski [6] suggested that the inhibitive nature of the molybdate anion was due to the reduction of the Mo^{6+} in the molybdate to Mo^{4+} during film formation. The reduction of the molybdate anion could provide additional oxygen anions that interfere with the ability of the chloride anion to react at the metal/film interface, possibly by blocking sites through which aggressive anions preferentially penetrate the film. Bairamov et al. [7] found that when Al was exposed to a solution containing sodium molybdate, the film formed was sufficiently thick to mask the Al oxide and metal signal.

These results corroborate the earlier work of McCune et al. [5] and the work of Stranick [3], who also found that molybdate was not incorporated into the passive film on Al, but rather was adsorbed onto the Al surface. McCune et al. concluded that it was incorporated into the composition of the film changing from being Mo-rich at the surface, to being Al-rich at the metal/film interface.

Moshier and Davis [9] found that the film formed on Al exposed to molybdate is dependent on its concentration and the solution pH. At low molybdate solution concentrations and near neutral pH, the film was thick and consisted of high concentration of MoO_2, whereas at higher molybdate solution concentrations, the film was a thin layer consisting mainly of molybdate. As the samples were polarized to more active potentials up to E_b, the chemistry of the passive film became less dependent on the solution concentration with molybdate dominating the film chemistry at the breakdown potential. This suggests that MoO_2 does not play a significant role in protecting the substrate. Rather, the important component is the molybdate layer that impedes the ingress of anions. This species not only limits the growth of the passive film by restricting the movement of oxygen and hydroxyl anions from penetrating the film and reaching the metal/film interface, it also restricts Cl^- anions and inhibits pitting.

Shaw et al. [10] studied the effect of molybdate treatment on the passivity of pure Al in chloride-containing environments. The passivity-enhancing treatment consisted of potentiostatically polarizing the specimens at a potential 300 mV more than the open circuit potential, E_{oc} (−500 mV vs SCE), for 2 h in 0.1 M sodium molybdate purged with pure nitrogen. Improved passivity was observed in the Mo-treated specimens even after vigorous rinsing and drying, indicating that the enhanced passivity results from the incorporation of Mo-containing species (Mo^{4+} and Mo^{6+}) into the three-dimensional oxide lattice, rather than adsorption on the surface.

Bairamov and Verdiev [11] studied the composition of surface films formed on aluminum when protected by molybdates from corrosion in aqueous chloride media. The surface condition plays a significant role in the protection of Al. If the adsorption of molybdate takes place onto an etched surface, reduction of Mo (VI) to Mo (IV) occurs, whereas no reduction occurs on an unetched surface.

In general, although there are many treatments which enhanced the behavior against pitting corrosion of several aluminum alloys, data reported to date suggest that the influence of molybdates is still unclear presenting various handicaps that limit their application on an industrial scale. The aim of this work is to study the effect of molybdate on the general corrosion and pitting behavior of aluminum composite and to find high performance anti-corrosion surface pretreatment for aluminum alloys and composites as an alternative to chromatation.

2. Experimental

2.1. *Materials*

The tested material is aluminum metal matrix composite, AA6061 T6 alloy-10% Al_2O_3 p (v/v), in the form of 60 × 30 mm taken from sheet of 3 mm thick. The nominal composition of the Al matrix was as follows (wt.%): 0.35 Cu; 0.95 Mg; 0.70 Fe; 0.50 Si; 0.15 Mn; 0.15 Cr; 0.25 Zn; 0.15 Ti; remainder Al.

2.2. *Specimen preparation*

Series of specimens were abraded to 800 finish with SiC grit papers, degreased in acetone, washed with distilled water, and dried in dry air. The specimens prepared under the following conditions:

Series 1: Full immersion

1. Pickling in KOH for 15 min followed by direct treatment in 0.1 N sodium molybdate solution for 3 h at pH 7 and pH 9 (the normal solution pH), respectively.
2. Immersion in boiling water for 1 h followed by treatment in 0.1 N sodium molybdate solution for 3 h at pH 7 and pH 9, respectively.
3. Pickling in KOH for 15 min followed by immersion in boiling water for 1h and then, treatment in 0.1 N sodium molybdates solution for 3 h at pH 7 and pH 9, respectively (KBMo3h).

Series 2: Electrochemical activation

1. Pickling in KOH for 15 min followed by direct treatment in 0.1 N sodium molybdate solution for 1 h followed by polarization step at −500 mV in the same Mo-solution for 1 h at pH 7 and pH 9, respectively.
2. Immersion in boiling water for 1 h followed by treatment in 0.1 N sodium molybdate solution for 1 h followed by polarization step at −500 mV in the same Mo-solution for 1 h at pH 7 and pH 9, respectively.
3. Pickling in KOH for 15 min immersion in boiling water for 1 h, treatment in 0.1 N sodium molybdate solution for 1 h followed by polarization step at −500 mV in the same Mo-solution for 1 h at pH 7 and pH 9, respectively (KBMoPz).

2.3. *Methods*

2.3.1. *Electrochemical impedance tests*

The corrosion behavior of the previously pretreated specimens was monitored using electrochemical impedance spectroscopy (EIS) after immersion in 3.5% NaCl solution open to air and at room temperature up to 60 days.

A three-electrode set-up was used with impedance spectra being recorded at the corrosion potential E_{corr}. A saturated calomel electrode (SCE) was used as the reference electrode. It was coupled capacitively to a Pt wire to reduce the phase shift at high frequencies. The

EIS were performed in the 0.01 Hz–65 kHz frequency range using Autolab PGSTAT 30 frequency response analyzer. The amplitude of the sinusoidal voltage signal was 10 mV.

2.3.2. *Polarization tests*

DC polarization tests of specimens previously immersed for 60 days in NaCl solution were made at a scan rate of 0.07 mV s^{-1} in an applied potential range from −0.15 V_{SCE} to 0.7 V_{SCE} with respect to E_{corr} using an Autolab PGSTAT 30 galvanostat/potentiostat. The exposed surface area was 2.54 cm^2. All curves were normalized to 1 cm^2.

2.3.3. *X-ray photoelectron spectroscopy*

Qualitative and quantitative analysis of the corrosion layers was made by X-ray photoelectron spectroscopy (XPS). A VG Escalab 210 XPS spectrometer, with a spherical sector analyzer and unmonochromatized Mg K_α radiation (E = 1253.6 eV) as excitation source, Fisons Instruments, Uckfield, UK, was used. The experimental condition for X-ray source was 15 kV and 20 mA. Spectra were obtained at a vacuum better than 10^{-8} mbar with a detection angle perpendicular to the surface; binding energies were determined with reference to Au $4f_{7/2}$, Ag $3d_{5/2}$ and Cu $2p_{3/2}$ and C 1s binding energy, 285.1 ± 0.1 eV, of hydrocarbon contamination, was used to compensate for charging effects. Qualitative analysis was made by deconvolving the spectra of the various elements with the Reduced Chi Squared method in order to obtain different peaks corresponding to the different species of each element. Quantitative analysis was made with the Schofeld method.

2.3.4. *Electron-probe microanalysis using EDS*

Scanning electron microscopic (SEM) images were obtained from a scanning electron microscope Model Stereoscan 250 MK3, Cambridge Instruments, UK. After SEM image observation, spot analyses of the surface components were carried out at a part of the surface where a corroded spot was observed. Electron microprobe analyses using the energy dispersive spectrometry (EDS) were performed using AN 10000 X-ray analyzer LZ-5 Link Analytical Limited, UK.

3. Results and discussion

3.1. *Series 1: Full immersion*

3.1.1. *Molybdate solution of pH 9 (without pH adjustment)*

The corrosion rates increased dramatically after 30 days of immersion in NaCl for all specimens. This is due to dissolution of aluminum ions from the matrix [12] causing localized corrosion.

3.1.2. *Molybdate solution of pH 7*

The specimens which were directly treated in molybdate showed a marked increase in the corrosion rates. This can be attributed to the adsorption of molybdate as bulky anionic species due to polymerization of MoO_4^{2-} in neutral media [12] which cannot be accommodated as a protective film at the surface of Al-composite and, hence, higher corrosion rates were observed.

The specimens that went through a preliminary oxide thickening step before molybdate treatment showed good corrosion resistance. The corrosion resistance was improved due to passivity enhancement resulting from incorporation of Mo-containing species Mo (VI) and Mo (IV) into the porous Al-oxide lattice [3, 6, 10, 11, 13–16]. However, SEM revealed a cracked surface layer after 60 days of immersion in NaCl (Figure 1). The best corrosion resistance was observed for the similar specimens which has been subjected to a pickling step before the oxide thickening process (Figure 2). SEM revealed an almost uniformly distributed Mo surface layer. Moreover, electron-probe microanalysis revealed a higher percentage of molybdenum at the material surface for the pickled specimens than for the

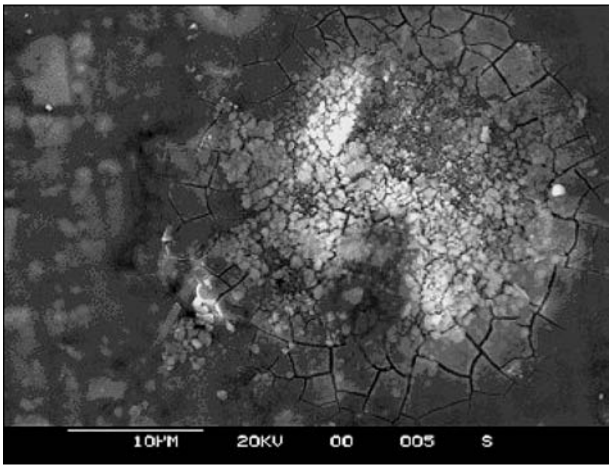

Fig. 1. SEM of oxide thickening followed by immersion in Molybdate pH 7 for 3 h after 60 days in NaCl.

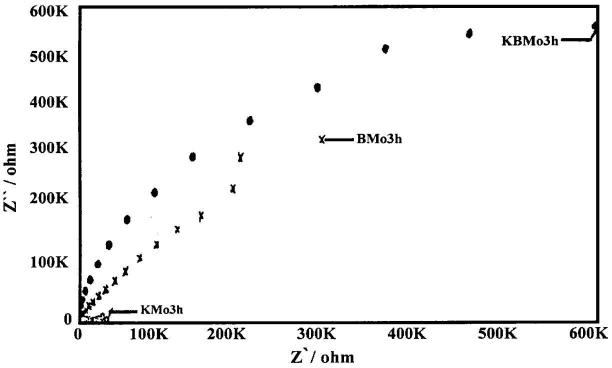

Fig. 2. EIS of full immersion at pH 7 after 60 days in NaCl KMo3h is the specimens only pickled, BMo3h is the oxide thickened specimens and; KBMo3h is the specimens pickled and oxide thickened.

non-pickled ones before exposure to NaCl. This observation can confirm the important role of pickling process to enhance the formation of a Mo-rich layer distributed uniformly over the material surface.

3.2. *Series 2: Electrochemical activation*

3.2.1. *Molybdate solution of pH 9 (without pH adjustment)*

The corrosion rates increased dramatically after less than 30 days of immersion in NaCl for the pickled and oxide thickened specimens. This can be attributed to dissolution of aluminum ions from the matrix at the alkaline pH [12] causing localized corrosion. Conversely, the specimens which were subjected to pickling followed by oxide thickening showed a distinct improvement in the corrosion resistance even after 45 days in NaCl. It seems that pickling and oxide-thickening processes together with electrochemical activation can form a highly protective Mo species.

3.2.2. *Molybdate solution of pH 7*

The specimens directly activated electrochemically in molybdate showed marked increase in the corrosion rates in NaCl. This increase can be attributed to the adsorption of molybdate as bulky anionic species consisting of polymerized MoO_4^{2-} [12]. The polymerized form MoO_4^{2-} cannot act as a protective film at the surface of Al-composite leading to higher corrosion rates.

The improvement of corrosion resistance for the specimens that went through an oxide-thickening step before Mo-activation can be attributed to the incorporation of Mo-containing species Mo (VI) and Mo (IV) into the porous Al-oxide lattice [3, 6, 10, 11, 13–16]. However, SEM revealed a cracked surface layer around the pits (Figure 3). The best protection was observed for the similar specimens which had been subjected to a pickling step before the oxide thickening process (Figure 4). Polarization tests showed a pitting auto repairing behavior even after 60 days of exposure to NaCl [17].

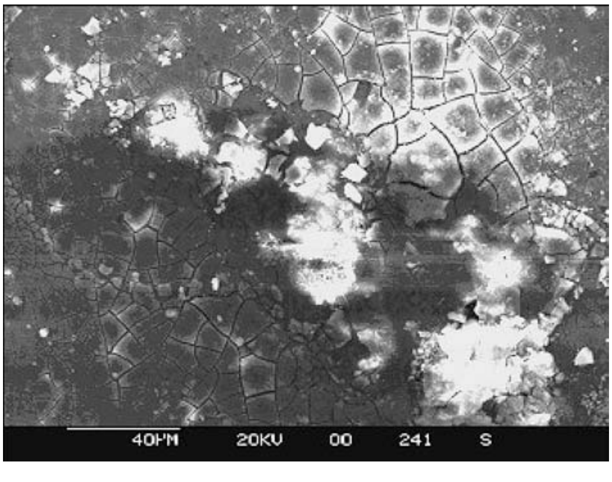

Fig. 3. SEM of oxide thickening followed by electrochemical activation in molybdate at pH 7 after 60 days in NaCl.

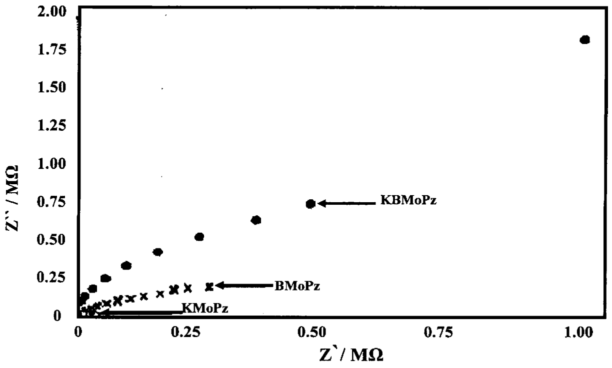

Fig. 4. EIS of chemical activation at pH 7 after 60 days in NaCl KMoPz is the specimens only pickled, BMoPz is the oxide thickened specimens and; KBMoPz is the specimens pickled and oxide thickened.

A comparison between the corrosion protection performance due to full immersion (series 1) and electrochemical activation (series 2) methods showed that:

- Generally, the treatment of Al in molybdate at pH 9 affects negatively the corrosion resistance irrespective of the techniques used for treatment (full immersion or electrochemical activation). This is due to dissolution of aluminum at high alkaline pH.
- Direct treatment of the pickled specimens in molybdate did not improve the corrosion resistance. This observation may be interpreted along the same lines as the directly treated specimens.
- Oxide thickening step plays a vital role in the corrosion protection mechanism. Molybdenum ions incorporated into the pores of the thick Al-oxide film form a highly protective layer.
- A combination between surface pickling and oxide thickening processes can present outstanding corrosion protection even after 60 days in NaCl. It seems that pickling produces a more uniform porous Al-oxide layer on the material surface. Consequently, the incorporated molybdenum ions are more uniformly distributed through out the pores. For this reason pickled specimens did not show any sign of cracking while non-pickled specimens showed many cracked surface areas (Figures 1 and 3).
- According to EIS results, electrochemical activation method provides a better corrosion resistance than full immersion method (Figure 5). The electrochemical activation method is more effective in reducing the number of pits and in enhancing the pitting auto repairing processes than the full immersion method. Potentiodynamic curves confirmed this observation where the difference between E_{pit} and E_{prot} amounted to 50 and 140 mV for KBMoPz and KBMo3h, respectively. Moreover, the passive current is 10 times lower for KBMoPz than for KBMo3h [17].

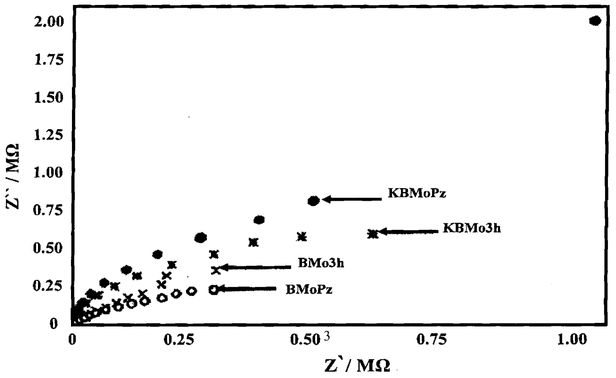

Fig. 5. Comparison between the full immersion and Electrochemical activation processes at pH 7 after 60 days in NaCl BMo3h is the oxide thickened specimens prepared by full immersion method, KBMo3h is the specimens picked and oxide thickened prepared by full immersion method, KMoPz is the oxide thickened specimens prepared by electrochemical activation method and; KBMoPz is the specimens picked and oxide thickened prepared by electrochemical activation method.

- According to the potentiodynamic results, molybdates improve the pitting resistance by shifting the breakdown, or pitting, potential to more noble values.
- XPS revealed a higher amount of molybdate as MoO_4^{2-} for the specimens of (KBMoPz) than (KBMo3h). Increasing the amount of molybdate at the surface of the specimens which were prepared by electrochemical activation could be the main reason for the superior corrosion resistance of such type of pre-treatment (Figure 6). However, the amount of chloride was found to be slightly higher in case of electrochemical activation specimens than in the case of full immersion ones (Figure 7 and Table 1).
- According to the microscopic examination, the tendency of MoO_4^{2-} for polymerization in neutral media [12] leading to bulky anionic species like $Mo_6O_{21}^{6-}$ was clear for the full immersion method. These species cannot be accommodated easily in the flawed regions of the surface film [13] and, hence, a relatively higher corrosion rate can be measured for the specimens treated by full immersion method. Conversely, the tendency MoO_4^{2-} to polymerize to bulky anionic molybdate species appears to be less for the electrochemical activation method than for the full immersion one.

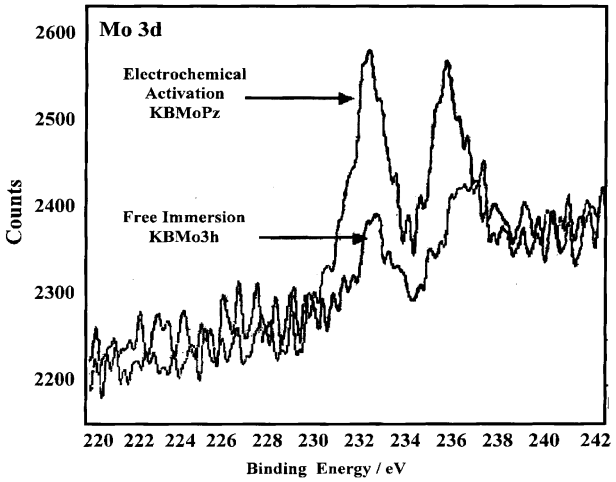

Fig. 6. Mo 3p of the corrosion layer formed after 60 days in NaCl.

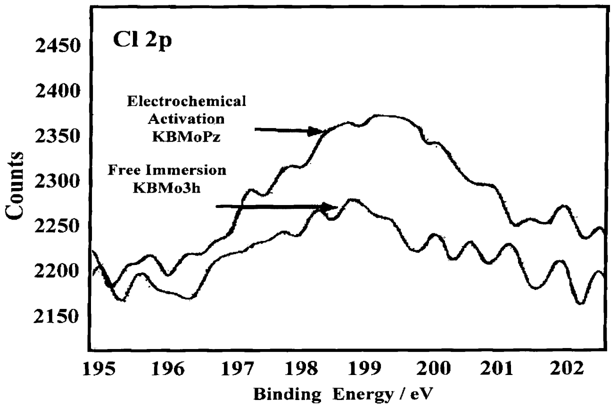

Fig. 7. Cl 2p of the corrosion layer formed after 60 days in NaCl.

Table 1. Mo/Al and Cl/Al atomic ratios using electrochemical activation and full immersion methods

Type of pre-treatment	Mo/Al Atomic ratio	Cl/Al Atomic ratio
1. Electrochemical activation (KBMoPz)	0.0120	0.0150
2. Full immersion (KBMo3h)	0.0054	0.0076

4. Conclusions

- Direct treatment in molybdate does not offer good corrosion protection in NaCl.
- Treatment in molybdate at pH 9 has a negative effect on the corrosion resistance due to dissolution of aluminum at high alkaline pH.
- Oxide thickening plays a vital role in the corrosion protection mechanism. Molybdenum ions can be incorporated into the pores of the thick Al-oxide layer to form a highly protective layer of MoO_4^{2-}.
- A combination between surface pickling and oxide thickening can present outstanding corrosion protection even after 60 days in NaCl.
- Pickling helps molybdate to distribute uniformly at the material surface, thus inhibition of the active surface sites and hence reducing the ratio of chloride ions, which is the main cause of pitting corrosion. Moreover, it plays an important role in activating pitting auto repair by enhancing the formation of a Mo-rich layer.
- The electrochemical activation method is faster and more effective than the full immersion method in enhancing the corrosion resistance of Al composites.

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