

Effects of Chromate and Molybdate Ions on Scratch Repassivation Behavior of Precipitation Hardened Aluminum Alloys

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The objective of the research presented is to understand inhibitor assisted repassivation of high strength aluminum 2000 and 7000-series alloys in aqueous environments rich in aggressive halides. We will examine the potential of chromate, molybdate and other selected inhibitors to form or stabilize protective surface oxides in harsh crack tip environments. This will lead to greater understanding of the mechanisms through which inhibitors can effect static and cyclic crack growth.

Crack tip film rupture events are thought to lead to hydrogen embrittlement and/or anodic dissolution in the crack tip. The ability of a stable film to regrow after film rupture is critical because it reduces the production of atomic hydrogen at the crack tip by limiting dissolution and hydrolysis of metal ions. The Al_2O_3 oxide is also a hydrogen permeation barrier which limits hydrogen ingress [1]. The reduction in atomic hydrogen on the surface of the metal and the presence of a permeation barrier decreases the amount of embrittling absorbed atomic hydrogen in the fracture process zone and slows anodic dissolution of Al. Introduction of chromate and molybdate [2, 3] to full emersion environmental fatigue crack propagation (EFCP) tests have shown that these inhibitors are capable of retarding the growth rate of cracks and that this inhibition is inhibitor concentration dependent.

Understanding effects of inhibitors on repassivation is crucial to understanding the effects of inhibitors on cyclic or static load environmental crack growth. The growth of oxides at the crack tip has been rationalized to be responsible for the frequency dependence of da/dN in the low frequency regime. f_{critUB} has been thought to indicate the frequency at which an oxide barrier is disrupted faster than it can repassivate or regrow to prevent Al^{3+} dissolution and/or the absorption of H_{ads} into the lattice. At low to moderate frequencies up to the critical frequency upper bound f_{critUB} inhibitors such as chromate and molybdate have been shown to reduce da/dN to levels below that seen in moist air and/or full immersion chloride environments [2, 3]. This presentation will showcase recent experimental evidence that inhibition of EFCP does not necessarily indicate a change in oxide repassivation alone. While some inhibitors have a great effect on repassivation current transients other EFCP effective inhibitors show very little effect on this parameter. We examine the regrowth of oxide films over freshly bared aluminum surfaces in the presence of aqueous inhibitors and chloride and try to elucidate other mechanisms through which inhibitors can reduce da/dN such as buffering the pH of crack tip solutions.

Scratch testing has been demonstrated in the literature to be useful in determining rates of metal dissolution, proton reduction, pitting potential, and oxide growth on many substrates including aluminum and aluminum alloys [4, 5], titanium [6], and steels [7, 8]. There is a very limited body of research addressing the influence of corrosion inhibitors such as chromate and molybdate on the processes that lead to the repassivation of scratched electrodes.

In this work we have examined the effect of inhibitor concentration, chloride concentration, as well as pH on the repassivation of AA2024 and AA7075. Scratch tests have been carried out on potentiostatically polarized

working electrodes and the current densities have been recorded. The potential dependence of the repassivation behavior has been explored over potentials ranging from -0.8 V (SCE) to -0.3 V (SCE). A variation on the traditional scratch depassivation experiment was carried by taking a fast, single frequency impedance measurement in the capacitive region of frequency response during repassivation. Capacitance measurements enabled the observation of oxide growth as protective oxide films repassivated the scratched electrode surface. Oxide rupture current transients during full emersion slow strain rate testing have also been analyzed. Nuclear reaction analysis has been used to observe the effect of chromate and molybdate on hydrogen absorption and diffusion. Depth profile XPS has been conducted to interrogate the chemistry of the repassivated oxides in the presence of inhibitors relative to hydrogen penetration distance.

Results to date have indicated that chromate is a very potent inhibitor of peak repassivation current densities as well as total charge per decade of time since depassivation. This result is evident for both AA2024 and AA7075 at a neutral pH of 6.5. The charge per decade is two orders of magnitude lower than uninhibited solution for AA2024 and one order of magnitude for AA7075. Inhibition of repassivation current by molybdate or either AA2024 or AA7075 has not been observed. This suggests that there are multiple mechanisms through which EFCP inhibition occurs given the results of Warner and Gangloff [2]. However, the buffering capacity of H_2MoO_4 may be responsible for the retarded EFCP observed or another as of yet undetermined mechanism might be responsible.

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