Cerium, Cobalt and Molybdate Cation Storage States, Release and Corrosion Inhibition when delivered from on Al-Transition Metal-Rare Earth Metal Alloys

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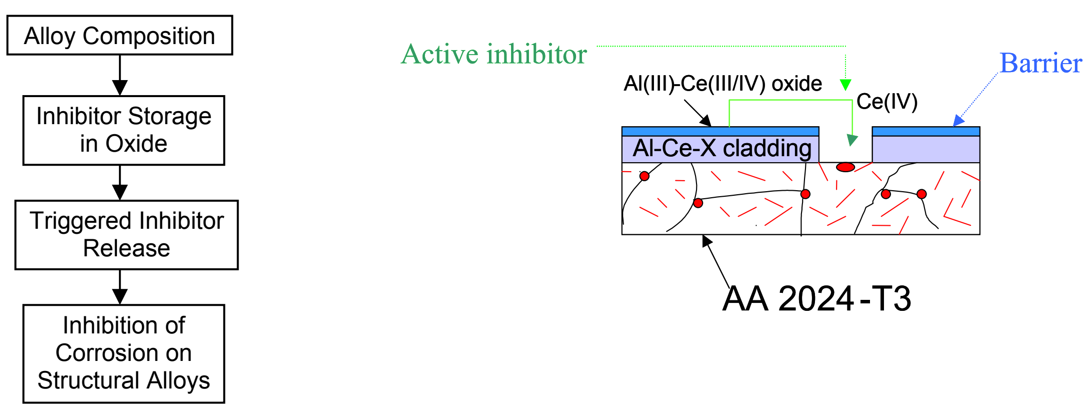
Aluminum and aluminum alloys can be protected against corrosion by various methods of surface modification (e.g., metal finishing, anodizing, chromate conversion coatings, metallic cladding with Alclad, corrosion protection compounds, and solution phase inhibitors). The desire to deploy environmentally compliant multi-functional coatings has created the need for new concepts that can protect Al-base precipitation age hardened alloys. A new generation of aluminum alloys with certain transition metals or lanthanides in an amorphous state provides an opportunity to create an environmentally compliant metal coating with multiple functions. Such metallic coatings not only can improve the resistance to localized corrosion, but also have the potential to provide a means for active corrosion protection at coating defects that expose underlying structural alloys (i.e., self-healing). The desired attributes of any new inhibitors (whether stored in a metal or polymer coating) are high capacity in the coating, high solubility in the aqueous phase over the coating when released, and high inhibiting efficiency. If such novel alloys are successful, the opportunity exists to create new multi-functional metallic cladding alloys that exhibit a broad range of corrosion functions.

One aspect of this MURI project involves the exploration of Al-based metallic glasses for coatings (metallic cladding) and the testing of different alloy compositions that could add functions ranging from improvement of corrosion barrier properties to sacrificial cathodic protection. Various cladding alloy compositions such as [Al-*TR* (Mo, Co, Ni, Fe, Cr) - *RE* (Ce, Gd, Y), Al-Cu-Mg-Ni (Ni promotes solid solubility of Cu and Mg) or Al-Sn (Sn promotes properties suitable for sacrificial anode applications)] are possibilities. The overall goal is to synthesize alloys with targeted composition to produce the desirable attributes and properties that achieve each function.

The active corrosion inhibition properties of a new Al-Ce-Co-Mo alloy recently synthesized at UVa is the focus of this specific project because of the possible release of Ce, Co and/or Mo cations from such an alloy. These ions serve as inhibitors. Moreover, synergistic effects of these three inhibitors could provide a viable chromate replacement. Three aspects must be studied and understood in order to provide the scientific foundations that enable metal coating with active inhibition qualities. We are investigating the storage, release and inhibition properties of active corrosion inhibitors delivered from these novel metallic coatings.

We are particularly interested in examining Ce(III) – Ce(IV), Co(II)-Co(III), and Mo(IV)-Mo(VI) storage and release from oxides formed over Al-Ce-*TR* alloys, such as $Al_{85.5}Co_7Ce_7Mo_{0.5}$, $Al_{85}Co_7Ce_7Mo$, $Al_{89.5}Co_3Ce_7Mo_{0.5}$ and $Al_{89}Co_3Ce_7Mo$. We are interested in exploring whether cerous or ceric ions, molybdate and cobalt(II) or cobalt(III) ions can serve as an active corrosion inhibitor by being stored and released from the oxide over the clad alloy, which serves as a reservoir for the inhibitor in the same way that a pigmented primer coating may contain an active corrosion inhibitor. We also are exploring the possible mechanisms of inhibition provided by these species.



(a) (b)

Figure 1(a). Schematic of requirements for active corrosion inhibition from a metal coating. 1(b). Schematic cross-section of the Al-(Ce, Co, Mo) cladding on AA2024-T3.

The storage states of metal cations in the oxide layer are being investigated by X-ray photoelectron spectroscopy (XPS). A typical survey scan of an amorphous Al-Ce-Co-

Mo alloy is shown in Figure 2. The surface sensitive XPS method reveals presence of Ce, Mo, and Co in the near surface region of these oxide covered alloys and thus confirms storage of inhibiting cations.

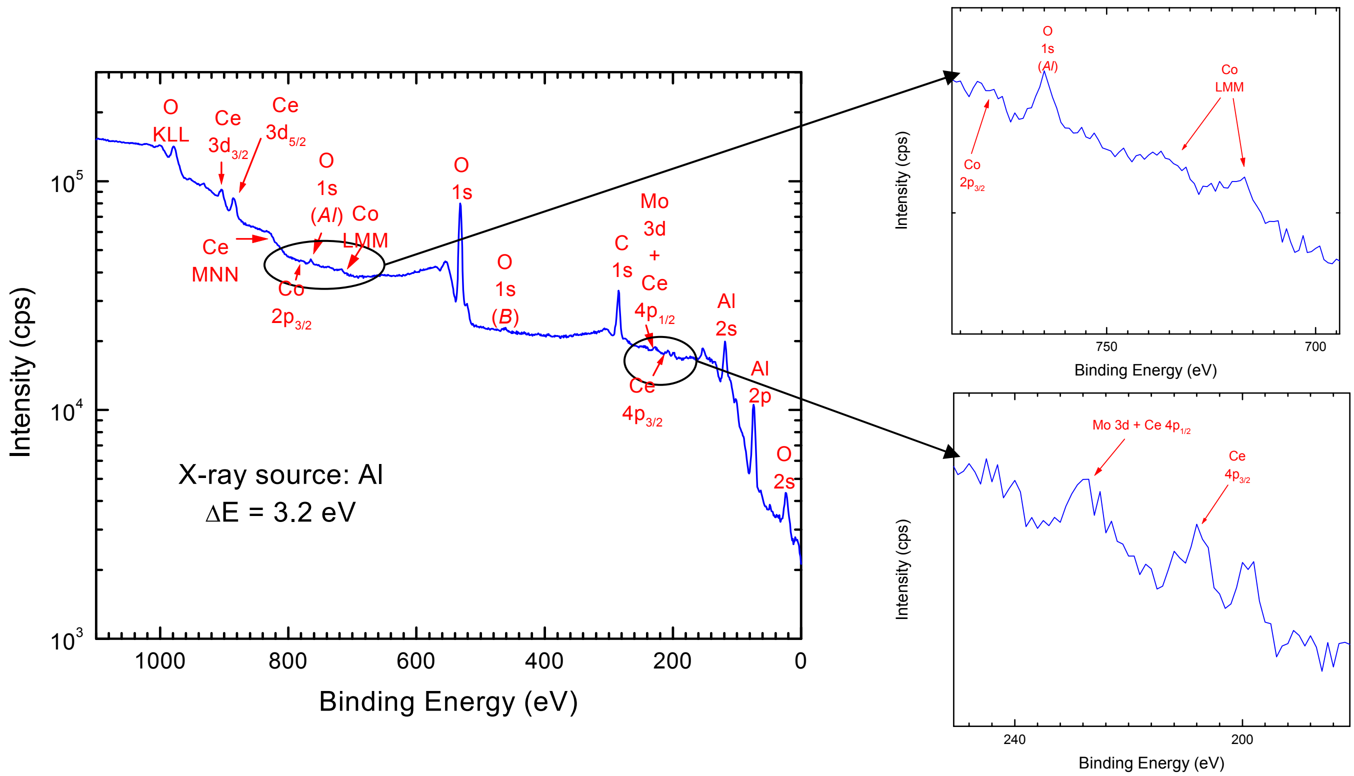


Figure 2. XPS spectrum of $Al_{89.5}Ce_7Co_3Mo_{0.5}$ alloy indicating storage of cerium, cobalt and molybdate inhibitors.

The possible benefits of the various candidate inhibitor ions potentially stored and released from an alloy coating have also been examined. Inhibition of corrosion of AA2024-T3 is under investigation using various electrochemical techniques that elucidate the inhibitor operation mechanism (potentiodynamic polarization, rotation disk electrode studies, open-circuit potential measurements and cyclic voltammetry). According to these studies, the most potent inhibitor ions are molybdate and cobalt (III), but cerium (III) and cobalt (II) also showed inhibiting capability. Specifically, molybdate and cobalt(III) inhibitors were found to alter anodic processes associated with pit stabilization on AA2024-T3, while cerium, cobalt(II), cobalt(III) and molybdate inhibitors all suppressed cathodic reactions essential to corrosion. Also, all inhibitors were found to suppress copper replating on AA2024-T3.

Future experiments will focus on inhibitor storage, more specifically on the determination of the valence state and composition of the oxides in the oxide layer of the alloy, and on the pH and anion dependent release of the inhibitor ions from the oxide. After full or alternate immersion of the alloy into solutions of different pH values, release will be determined by monitoring solution composition using UV-VIS or AA spectroscopy, and depletion of enriched solute initially in the oxide will be assessed by comparing XPS conducted before and after release.

The technological output will be a better understanding of whether an Al-Co-Ce-Mo metallic coating can provide the storage/release/inhibition attributes necessary to serve as a coating that functions as substrate capable of supplying active corrosion inhibition in much the same way as an organic primer containing active inhibitor functions.

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