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XANES Investigation of Cerium as an Inhibitor for Al Alloys

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Cerium ions have been found to be effective corrosion inhibitors for aluminum, mild steel and zinc [1-5]. Development of cerium ions as corrosion inhibitors is particularly desirable as they provide a non-toxic alternative to carcinogenic chromates. The mechanism of interaction between cerium ions and oxide films on aluminum has been studied using XANES (X-ray Absorption Near Edge Structure [6,7]. The Ce L_3 x-ray absorption edge shows a clear difference between the 3- and 4-valent states. The results reported here show the valence state of cerium in oxide films on aluminum alloys formed by different treatments in solutions containing Ce^{3+} ions.

Measurements were made in the fluorescence mode with x-rays incident at small angles close to the critical angle (~6mrad). The x-ray absorption signal is calculated by taking the ratio of the intensity ot the fluorescent x-ray signal to that in the incident beam (I_f/I_0). Fluorescent x-rays are emitted when atoms which have absorbed monochromatic x-rays relax back to the ground state. X-ray absorption edges for standard compounds ($CeCl_3.7H_2O$ and CeO_2) were measured in transmission geometry by taking the logarithm of the ratio of the incident to the transmitted x-ray intensity ($\log(I_0/I)$).

Specimens of Alloy 1100 (commercially pure aluminum), 2024 (Cu-containing), 2090 (Li-containing) and 7075 (Zn-containing) 5cm x 2.5cm x 0.5cm were lapped by an automatic lapping machine to a 0.03μm finish. Before treatment, the samples were lightly polished with 1μm diamond paste and rinsed with deionized water.

The specimens shown in Fig.1 were immersed in 4mM $CeCl_3$ for 7 days. 1100 shows predominantly 3-valent cerium (this can be seen by comparison with $CeCl_3$) whereas the other alloys show a stronger higher energy peak associated with significant 4-valent cerium (*c.f.* CeO_2). The potentials for the alloys in the aerated Ce(III) chloride solutions were all in the range -600 mV to -700 mV(SCE) except for the 2024 which was slightly higher. The potential for the Cu was in the vicinity of -200 mV whereas that for Zn was below -1200 mV. The film formed on copper contains 3-valent cerium whereas the film on Zn contains 4-valent cerium. This suggests that the metallic substrates exert no direct galvanic effect on the Ce(III)/Ce(IV) couple, rather it is other effects such as the extent of pH increase at local cathodes and codeposition with dissolved corrosion products which contribte to the conversion of the +3 valent Ce to +4.

Subsequent exposure to NaCl converts all the cerium to the 4-valent state. The weaker signal and higher noise level indicates that much of the cerium has been lost from the films.

Fig.2 indicates the effect of different surface treatments on cerium incorporation in the oxide film on Alloy 1100. The freshly polished and air oxidized surfaces give a mixture of 3- and 4-valent cerium (the air-oxidized surface was held in an oven at 100°C for 1 hour). The etched and steam-aged (held over boiling deionized water for 12 hours) surfaces give predominantly 4-valent cerium.

Conclusion

The alloy and the surface preparation have a strong effect on the incorporation of cerium ions in the oxide film on aluminum alloys.

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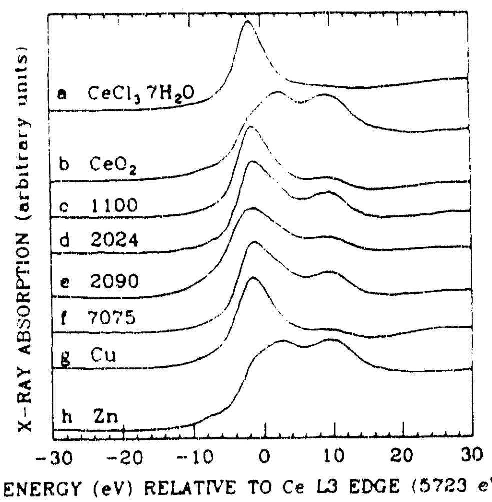

Fig.1 Cerium L_3 x-ray absorption edges of powdered samples measured in transmission: (a) $CeCl_3.7H_2O$, (b) CeO_2. Films formed on aluminum alloys by immersion in 4mM $CeCl_3$ measured in fluorescence geometry: (c) 1100, (d) 2024, (e) 2090, (f) 7075, (g) pure Cu, (h) pure Zn. The data are normalized to give the same peak height.

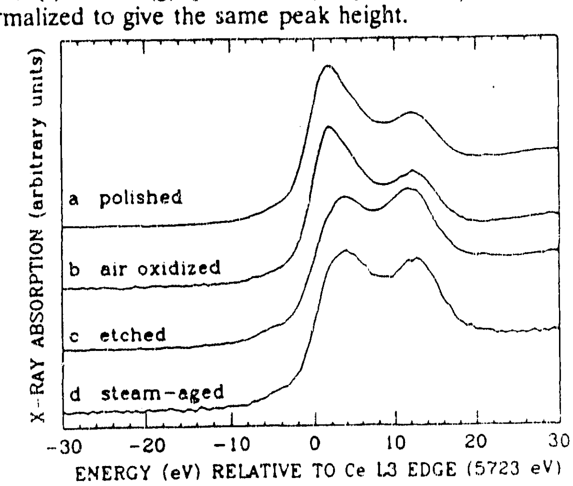

Fig.2 Cerium L_3 x-ray absorption edges measured for films on aluminum Alloy 1100 after immersion in 4mM $CeCl_3$ for 7 days following different pre-treatments: (a) freshly polished, (b) air-oxidized, (c) etched, (d) steam-aged.

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Cerium ions are under investigation as possible replacements for toxic chromates. The use of cerium ions as corrosion inhibitors for aluminum alloys is investigated using XANES (x-ray absorption near edge structure). On immersion in a dilute solution of cerium ions, cerium is incorporated into the oxide films on aluminum alloys in either the 3- or 4-valent state depending upon the alloy and on the surface preparation.

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