Deposition of a mixed cerium oxide CeO$_2$/Ce$_2$O$_3$ thin film for corrosion protection of Al

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**Introduction**

It is accepted that thin films composed of a mixture of cerium oxides (Ce$^{3+}$, Ce$^{4+}$) exhibit high potential for corrosion protection of metallic substrates (Al, stainless steel). In order to evaluate this potential, deposition of cerium oxide thin films (~100 nm) on Al substrates has been carried out on a lab-scale chamber by unbalanced reactive DC magnetron sputtering at 50 W. Measurement of the transition curve of the Ce target helped to define the regions of interest for subsequent depositions. XRD analysis (Siemens D 5000) allowed to check crystallinity of the deposited films. Chemical characterization of the bulk of the films was obtained using XPS (PHI VersaProbe 5000) with a C$_{60}^+$ erosion gun for depth profiling.

**Experimental details**

- unbalanced reactive DC MS
- base pressure ~ 5 x 10$^{-6}$ Torr
- working pressure 5 mTorr
- Ar-O$_2$ (up to 50%) mixture
- cathode power ~ 50 W
- target-substrate distance 10 cm
- polished Al 2024 substrates

**Chemical characterization (XPS analysis)**

- Deposition in Ar-O$_2$ mixture in metallic mode (2.5 % O$_2$)
- Ce$^{3+}$/Ce$^{4+}$ on the surface and Ce$^{3+}$ in the bulk

- Deposition in Ar-O$_2$ mixture in transition mode (5 % O$_2$)
- Ce$^{3+}$ & Ce$^{3+}$/Ce$^{4+}$ on the surface and Ce$^{3+}$ in the bulk

- Deposition in Ar-O$_2$ mixture in poisoned mode (20 % O$_2$)
- Ce$^{3+}$ & Ce$^{3+}$/Ce$^{4+}$ on the surface and Ce$^{3+}$ in the bulk

**Crystallographic constitution (XRD analysis)**

**Corrosion test**

- Anodic polarization (100mV/min, NaCl 0.1M)

- Transition curve

\[ \text{Partial pressure of O}_2 \text{ mTorr} \]

\[ \text{Voltage (V)} \]

- Corrosion test

- Metallic mode
- Poisoned mode
- Transition mode

- as received Al
- polished Al
- poisoned mode
- metallic mode
- transition mode

**Transition curve**

- 5 mTorr, constant current 190 mA (~50 W)

- Corrosion test

- Metallic mode
- Poisoned mode

- Deposition in Ar-O$_2$ mixture (in different modes of transition curve) allowed to obtain amorphous cerium oxide thin films enriched with Ce$^{4+}$ in the surface region, most likely due to post-deposition oxidation. The bulk of the films contains predominantly Ce$^{3+}$.

- Varying degree of propagation of post-deposition oxidation (~ 5 nm for metallic mode, ~ 10 nm for poisoned and transition modes) can be attributed to different microstructure of the films. Investigation of the film microstructure would clarify this consideration.

- Anodic polarization curves display that corrosion current is most efficiently decreased for cerium oxide thin films deposited in poisoned mode. These preliminary results should be confirmed by measurement of cathodic polarization curves.