Elaboration and characterization of thin solid films containing cerium

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Abstract : Cerium oxide films are widely studied as a promising alternative to Cr(VI) based pre-treatments for the corrosion protection of different metals and alloys. Cathodic electrodeposition of Cerium containing thin films was realised on TA6V substrates from a Ce(NO3)3,6H2O and mixed water-ethyl alcohol solutions at 0.01 M. Experimental conditions to obtain homogeneous and crack free thin films were determined. The deposited cerium quantity appears proportional to the quantity of electricity used, as indicated by the Faraday law. Subsequent thermal treatment lead to a CeO2 coating, expected to provide an increase of TA6V oxidation resistance at high temperatures. The deposits were characterized by differential scanning calorimetry (DSC), optical and scanning electron microscopies.Titanium and its alloys have been considered as one of the best engineering materials for use in industrial application due to their high specific strength, good corrosion resistance and biocompatibility [1-3].However, a major problem of titanium alloys is an insufficient wear resistance and serious oxidation at high temperature [4,5].To combat this problem, conversion coatings are widely used as part of the corrosion protection system [6]. The use of rare-earth compounds particularly cerium compounds have attracted significant attention for corrosion protection of metals and alloys as a result of new environmental regulations to replace toxic compounds [7, 8]. Cathodic electrodeposition has been used because of the low cost of equipment and of precise control of deposited thickness [9,10]. The focus of this study is on cerium based conversion coatings, wich have shown promise as potential replacements for chromates [11,12]. In the present work, an electrodeposition technique was used to get, in one step, thin cerium containing films over all surfaces of TA6V samples. The deposits were then submitted to a thermal treatment under argon in order to get a CeO2 coating, the aim being to later study the behaviour of such a coated material under high temperature oxidation conditions.The electrochemical bath was a 0.01 M Ce(NO3)3 solution, obtained by dissolving commercial cerium nitrate (Ce(NO3)3, 6H2O, 99.99% purity) in water 50 vol.% ethyl alcohol. Electrodeposition was realised using a classical three electrode experimental set-up, described elsewhere [13,14], including a TA6V sample as cathode, a platinum grid counter electrode and a saturated calomel electrode (SCE) as reference. Deposition experiments were carried out in galvanostatic mode, current density varying from j= -2 to - 0.05 mA cm-2, at ambient temperature and without stirring. Deposition time was varied from 100 to 7200 s. The variation of the potential versus time was recorded during deposition. After electrodeposition, samples were rinsed with ethyl alcohol and air dried for at least a night before further use or analysis. These experimental conditions were chosen from previous work [14] and were expected to provide thin films with a thickness in the range 50–500 nm.The aim of this work was to determine adequate parameters for cathodic electrolytic deposition, on TA6V substrate, of cerium hydroxide films from mixed water–ethyl alcohol solutions to obtain, after a thermal treatment, thin CeO2 films(<500 nm), suitable for high temperature purposes. The deposit weight and hence the deposit thickness was shown to increase with current density at a constant deposition time. However, low current densities (-0.2 mA.cm-2) promoted the formation of thin, crack-free films (which was not the case for higher current densities). The deposited cerium quantity appears proportional to the quantity of electricity used, as indicated by the Faraday law. Microscopic observations (-0.2 mA.cm-2) revealed that formed cerium hydroxide films are uniformly deposited all over the sample surfaces. The results of the DSC analysis are in perfect concordance with the literature. This study thus illustrates that electrolytic deposition can be used to obtain thin and uniform cerium films over a metallic substrate used as the cathode. High temperature oxidation experiments are currently performed on coated specimens. First results are quite promising.

Keywords : electrodeposition, Cerium oxide, Cthodic deposit, Titanium alloy.