

ELECTRO-DEPOSITION OF CERIUM THIN FILM COMPOUND, ELABORATION AND CHARACTERISATION

S. Hamdi, R. Siab and G. Bonnet¹

Centre Universitaire El Tarf, B.P. 72, El-Tarf 36000, Algeria

¹Laboratoire le LEMMA, Université de La Rochelle, France
rachsiab@yahoo.fr

(Received 5 January 2009 - Accepted 11 June 2009)

ABSTRACT

Cerium oxide films are widely studied as a promising alternative to the toxic hexavalent Chromium Cr(VI) based pre-treatments for the corrosion protection of different metals and alloys. Cathodic electro-deposition of Cerium compound thin films was realised on Ti alloy (TA6V) substrates from a $Ce(NO_3)_3 \cdot 6H_2O$ in water-ethyl alcohol solutions at 0.01 M. Experimental conditions to obtain homogeneous and crack free thin films were determined. The deposited cerium quantity, as expected, is proportional to the used electric charge, following the Faraday law. Subsequent thermal treatment led to a CeO_2 coating, which is expected to increase the TA6V oxidation resistance at high temperatures. The deposits were characterized by Differential Scanning Calorimetry (DSC), optical and scanning electron microscopies.

Keywords: electrolytic deposition, cerium oxide cathodic deposit, titanium alloy

INTRODUCTION

Chromium (VI) compounds are largely used to provide an improved protection layer on many metallic alloys, despite its toxic properties. The use of rare earth (RE) salts is nevertheless studied as an environmentally friendly alternative to the use of Cr (VI) based pre-treatments. An enhancement of the corrosion resistance by many treatments, on different alloys like aluminium alloys (Kahraman *et al.*, 2007; Gonzalez & Mirza-Rosca, 1999; Kathy, 1996), zinc alloys (Zufang, 1999; Schutz, 1993; Baudrond, 2005; Bethencourt *et al.*, 2004; Decroly & Petitjean, 2005) or steels (Zhou *et al.*, 1996; Stefanov *et al.*, 2004; Lytle *et al.*, 1995) have been reported. The deposition of a metallic layer or stable oxide directly on the alloy can be an efficient solution to improve the corrosion resistance at high temperature. For example, Y. Shida and Anada showed that addition of Nb, W or Mo into TiAl intermetallics increased their resistance to high-temperature oxidation (Fahrenholtz *et al.*, 2002). From a general point of view, the choice of a deposition technique must take into account several characteristics: the deposition temperature has to be low enough to keep the mechanical

properties of the metallic matrix, the technique must allow coating complex shaped substrates, with a controlled thickness and it must be as cheap as possible.

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 atmosphere in order to get a CeO_2 coating, the aim being to study, later, the behaviour of such coated material under high temperature oxidation conditions.

EXPERIMENTAL PROCEDURES

In all experiments wafers, of 10mm in diameter and 2mm in thickness, were cut from a commercial TA6V alloy rod (Ti-6wt.% Al-4wt.%V), a 1.5mm hole was made for suspension. Samples were polished by a 600 grade SiC paper ($3\mu\text{m}$ diamond grain), ultrasonically cleaned in acetone, water and ethanol and then dried with pulsed warm air before use. A chemical etching by Kroll's reactant (2 vol.% hydrofluoric acid and 3vol.% nitric acid in water) ,the developed edges showed that TA6V alloy presents a two-phase structure (95.4% hexagonal α -phase and 4.6% cubic β -phase) (see Fig. 1), that explain the wide use of this titanium alloys, being a compromise between α -alloys, having the best weldability, and the combination of $\alpha+\beta$ alloys, giving the best mechanical resistance.

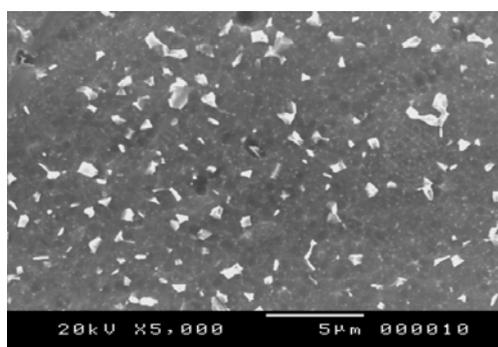


Figure 1. SEM micrograph showed that TA6V alloy presents a two-phase structure (95.4% hexagonal α -phase and 4.6% cubic β -phase).

Experimental set-up for cathodic electrodeposition

The electrochemical bath was a 0.01 M $\text{Ce}(\text{NO}_3)_3$ solution, obtained by dissolving commercial cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.99% purity) in water solution with 50 vol.% ethyl alcohol. Electrodeposition was realised using a classical three electrode experimental set-up, described elsewhere (Zhitomirsky & Petric, 2001; Brossard *et al.*, 2004) 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, constant 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 in desiccator for at least one night before further use or analysis.

These experimental conditions were chosen from previous work (Brossard *et al.*, 2004) and were expected to provide thin films.

Deposited and thermally treated films characterisation

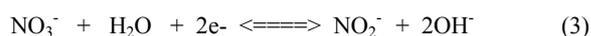
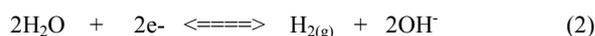
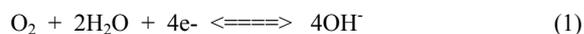
Different analytical techniques have been used to characterise the deposited film and its behaviour during thermal conversion treatment. Deposit morphology was observed by Optical and Scanning Electron Microscopy's (OM, SEM). A deposit formed at $j = -0.2 \text{ mA cm}^{-2}$ during 7200 s was scraped off from the substrate surface, the scraped layer was also used for differential scanning calorimetry (DSC 2010/2920 cell, TA instruments-universal analysis 2000): it was placed in an aluminium nacelle and heated from 40 to 560 °C at 10 °C min^{-1} , then cooled down to room temperature and finally submitted to a second thermal cycle. The quantity of deposited cerium versus deposition time has been determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES). Deposits formed at $j = -0.2 \text{ mA cm}^{-2}$ for 100–7200 s duration were dissolved directly from the substrate in a water 5 vol.% nitric acid solution and the obtained solutions were analysed following the usual procedure for this technique.

RESULTS AND DISCUSSION

Electrodeposition

Electrochemical mechanism during cathodic deposition has been widely discussed in the literature (Balasubramaniam *et al.*, 1999; Wang & Golden 2003; Golden & Wang, 2003; Li & Thompson, 1999) . Two steps have to be distinguished (Zhitomirsky, 2002; Gal-Or *et al.*, 1991; Peulon & Lincot, 1998).

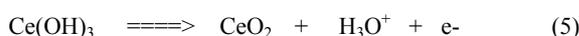
The first step corresponds to the cathodic generation of hydroxyl ions, OH^- , by reduction of O_2 , H_2O or NO_3^- , *etc.*...



The second one should be the precipitation reaction of Cerium hydroxide. The formation of hydroxyl ions at the cathode leads to local increase of the pH at the surface that promotes the formation of a $\text{Ce}(\text{OH})_3$ precipitate (Eqs.(4)) (Li & Thompson, 1999).



The Cerium oxide film results then from the oxidation of $\text{Ce}(\text{OH})_3$ (Eq. (5)) (Balasubramaniam *et al.*, 1999; Qi Wang & Golden, 2003; Golden & Qi Wang, 2003; Li & Thompson, 1999)



The electrochemical formation mechanism of these oxide films is really complex. Li and Thompson (1999) suggested that the deposition of the solid film proceeded through a nucleation and growth process. In this study, a low density current was used (-0.05; -0.1; -0.2 $\text{mA}\cdot\text{cm}^{-2}$). Results in the literature (Rane *et al.*, 2005), suggests that rinsing with ethanol could eliminate more nitrates than water or that their decomposition is too weak to be recorded.

Polarization experiments

Cathodic polarization curves for TA6V in a mixed water–ethanol solution of cerium nitrate, without stirring, are shown in Fig. 2. Addition of ethyl alcohol reduces the total dielectric constant of solvent and decreases the double layer thickness promoting particle coagulation and gel formation (Zhitomirsky & Petric, 2001). The polarization curves obtained with unstirred solution can be divided in different potential domains. For the first domain (Fig. 2a, 2b), at potentials between -0.2 to -1.1 V/SCE, the low current densities observed correspond to reduction of dissolved oxygen (Eq. (1)).

In the second domain from -1.1 to -1.6 V/SCE, the cathodic current density increases quickly: the reaction taking place being reduction of water to form H_2 (Eq. (2)).

From -1.6 to -1.8 V/SCE, current density increases slowly (like a steady state) value ($j = -0.8 \text{ mA cm}^{-2}$). This phenomenon is attributed to the surface blocking by a formed film by the precipitation of hydroxyl ions previously produced. Further continuation of potential scan towards cathodic potential results in an increase of current density due to hydrogen evolution reaction (Eq. (2)). At the same time, strings of H_2 gas bubbles start being observed. This feature may indicate that the film previously formed on the metal surface undergoes local breakdown manifested in gas bubbles, creating sites of stronger reduction current.

Galvanostatic deposition

Experiments performed on galvanostatic mode, without stirring, varying cathodic current density, revealed deposit formation even for very low current densities, showing that the local rise in pH responsible for the precipitation is effective. The effect of current density

on film morphology has been investigated in order to obtain homogeneous and crack free thin films. For a current density of $-1 \text{ mA}\cdot\text{cm}^{-2}$, the film formation is rapid and very important cracks can be observed in scanning electron microscopy (see Fig. 3).

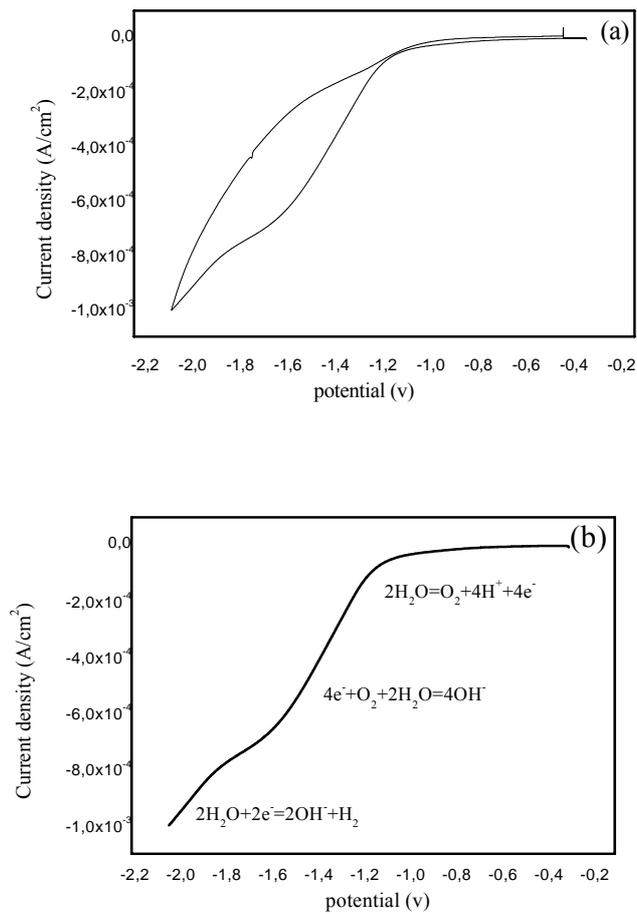


Figure 2. Cyclic voltammetry curves obtained with TA6V substrates with a water-ethyl alcohol solutions $\text{Ce}(\text{NO}_3)_3$, $6\text{H}_2\text{O}$ at $0.01 \text{ mol}\cdot\text{L}^{-1}$, (10 mV/s).

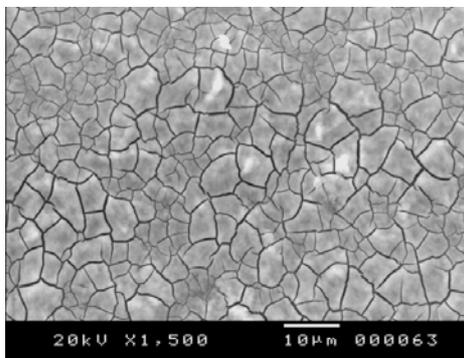


Figure 3. SEM micrograph of cerium alloy deposit ($j = -1 \text{ mA}\cdot\text{cm}^{-2}$, deposition time 1800s), showing the cracking of the film.

To avoid the cracking formation, smaller intensity values, ranging from -0.05 to $-0.2 \text{ mA}\cdot\text{cm}^{-2}$ were then selected in order to lower the electrodeposition rate. Fig. 4 gives the variation of potential versus time deposition, at $j = -0.05$, -0.1 and $-0.2 \text{ mA}\cdot\text{cm}^{-2}$. In every case, a very quick decrease of potential is observed in the first few seconds, corresponding to current stabilisation, then a transition period and, finally, a regular decrease of potential as film thickens.

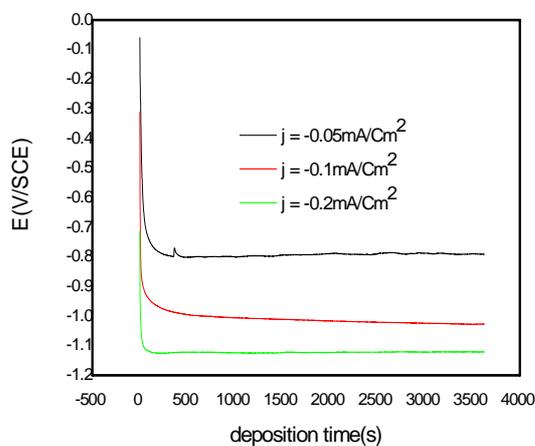


Figure 4. Variation of potential vs. time during cathodic deposition at constant $j = -0.05$, -0.1 and $-0.2 \text{ mA}/\text{cm}^2$.

An homogeneous film (Fig. 5) is obtained after a 1800 s deposition time under $j = -0.2 \text{ mA}\cdot\text{cm}^{-2}$, this current density has been chosen for further characterisation.

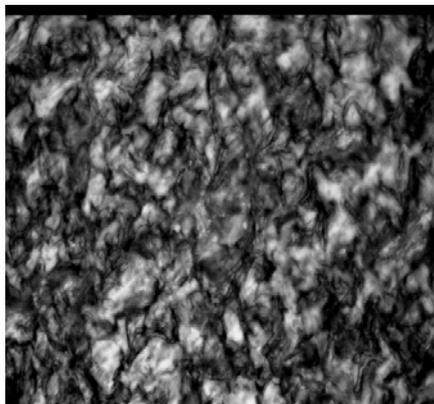


Figure 5. Optical micrograph of cerium alloy deposit ($j = -0.2 \text{ mA.cm}^{-2}$).

Electrodeposited cerium quantity

The quantity of deposited cerium versus deposition time, at $j = -0.2 \text{ mA.cm}^{-2}$ current density, dissolved in HNO_3 , has been determined using ICP-OES. A linear variation of cerium quantity with time can be observed on Fig. 6. The deposited cerium quantity appears proportional to the used electric charge, according to Faraday's law. This variation provides an easy control of the film thickness, for the fixed conditions. Moreover, these results are close to those obtained by Zhitomirsky and Petric (2001) on Pt substrates and confirm that mechanism and electrodepositing rate are independent of metallic substrate nature.

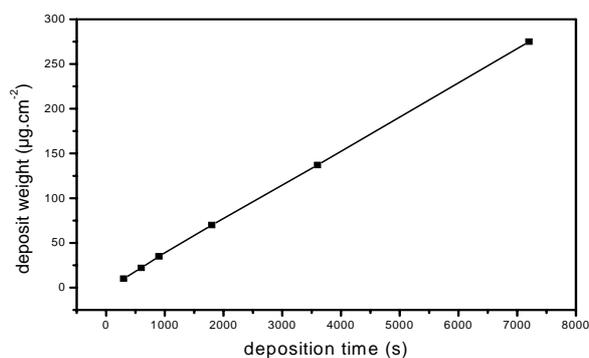


Figure 6. ICP-OES measurements of the deposited cerium amounts vs. time (current density $j = -0.2 \text{ mA.cm}^{-2}$).

Effect of heat treatment

Heat treatment under Argon atmosphere was applied on deposited films in order to promote dehydration (Creus *et al.*, 2006), inter-diffusion and adhesion (Zhitomirsky & Petric, 2000) of the deposit on metallic substrate. Results of thermal analysis (DSC) of $\text{Ce}(\text{OH})_3$ powder are presented in Fig. 7. It can be observed that two exothermic peaks, flat one at 200 and sharp one at 450°C appear during the first heating. Cooling curve and second heating curve demonstrated that all the transformations are irreversible. The presence of a weak exothermic peak around 450°C during the second heating indicates that the deposit crystallization is incomplete (Hamlaoui *et al.*, 2009). These results are close to those obtained by Zhitomirsky and Petric (1999), studied by Differential Thermal Analysis (DTA). In fact this author observed two successive weight changes at different temperatures. The first one, below 200 °C, seem to originate from the water loss associated with $\text{Ce}(\text{OH})_3$. The second one, taking place at approximately 450 °C, was related to the conversion of hydroxide into oxide. This sequence appears satisfactory to interpret the two exothermic peaks observed in this analysis. The extension of the Pt result to TA6V explains satisfactorily the two exothermic peaks observed in the DSC analysis of Fig. 7.

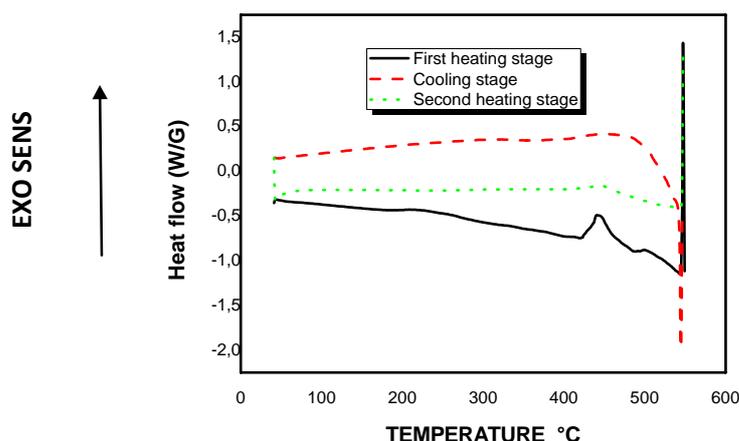


Figure 7. DSC analysis of the deposit grinding from 40 to 560 °C at 10 °C.min⁻¹.

CONCLUSION

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 CeO_2 films, 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 ($-0.2 \text{ mA}\cdot\text{cm}^{-2}$) promoted the formation of thin, crack-free films (in opposition to higher current densities).

The deposited cerium quantity appears proportional to the used electric charge. Microscopic observations ($-0.2 \text{ mA}\cdot\text{cm}^{-2}$) revealed that the cerium hydroxide films formed 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.

ACKNOWLEDGEMENTS

The authors are greatly thankful to M. Bordes (C.C.A la Rochelle University) for her contribution to Scanning Electron Microscopy analysis and to S. Cohendoz (Laboratoire le Lemma la Rochelle University) for his valuable help on DSC analysis.

REFERENCES

- Balasubramaniam, M., Melendres C.A., Mansour, A.N. 1999. An X-ray absorption of the local structure of cerium in electrochemically deposited thin films. *Thin Solid Films*, 347: 178-183.
- Baudron, D. 2005. Conversion coatings for aluminium and magnesium. *Plating and Surface Finishing*, 92(1): 30-35.
- Bethencourt, M., Botana, F.J., Cano, M.J., Marcos, M. 2004. Advanced generation of green conversion coatings for aluminium. *Applied Surface Science*, 238: 278-281.
- Brossard, J.M., Bonnet, G., Balmain, J., Creus, J. 2004. Characterization of thin solid films containing yttrium formed by electrogeneration of base for high temperature corrosion applications. *Surf. Coat. Technol.*, 185 : 275-282.
- Creus, J., Brezault, F., Rebere, C., Gadouleau, M. 2006. Synthesis and characterization of thin cerium oxide coatings elaborated by cathodic electrolytic deposition on steel substrate. *Surf. Coat. Technol.*, 200: 4636-4645.
- Decroly, A., Petitjean, J.P. 2005. Study of the deposition of cerium oxide by conversion on to aluminium alloys. *Surface & Coatings Technology*, 194(1): 1-9.
- Fahrenholtz, W.G., O'Keefe, M.J., Zhou, H., Grant, J.T. 2002. Characterization of cerium-based conversion coatings for corrosion protection of aluminium alloys. *Surf. Coat. Technol.*, 155: 208-213.
- Gal-Or, L., Silberman, I., Chaim, R. 1991. Electrolytic ZrO_2 coating. I. Electrochemical aspects. *J. Electrochem. Soc.*, 138: 1939-1942.
- Golden, T.D., Qi Wang, A. 2003. Anodic electrodeposition of cerium oxide thin films. *J. Electrochem. Soc.*, 150: C621-C624.
- Gonzalez, J.E.G., Mirza-Rosca, J.C. 1999. Study of the corrosion behavior of titanium and some of its alloys for biomedical and dental implant applications. *J. Electroanal. Chem.*, 471: 109-115.
- Hamlaoui, Y., et al. 2009. Investigation of electrodeposited cerium oxide based films on carbon steel and of the induced formation carbonated green rusts. *Materials Chemistry and Physics*, 113: 650-657.
- Kahraman, N., Gulenc, B., Findik, F. 2007. Corrosion and mechanical-microstructural aspects of dissimilar joints of Ti-6Al-4V and Al plates. *Int. J. Impact Eng.*, 34: 1423-1432.

- Kathy, W. 1996. The use of titanium for medical applications in the USA. *Mater. Sci. Eng.* 213A: 134-137.
- Li, E.B., Thompson, G.E. 1999. *Situ* atomic force microscopy studies of the deposition of cerium oxide films on regularly corrugated surfaces. *J. Electrochem. Soc.*, 146: 1809-1815.
- Lytle, F.W., Greegor, R.B., Bibbins, G.L., Blohowiak, K.Y., Smith, R.E., Tuss, G.D. 1995. An investigation of the structure and chemistry of a chromium-conversion surface layer on aluminium. *Corr. Sci.*, 37(3): 349-369.
- Peulon, S., Lincot, D. 1998. Mechanic study of cathodic electrodeposition of zinc oxide and zinc hydroxychloride films from oxygenated aqueous zinc chloride solutions. *J. Electrochem. Soc.*, 145 : 864-874.
- Qi Wang, A., Golden, T.D. 2003. Anodic electrodeposition of cerium oxide thin films. *J. Electrochem. Soc.*, 150: C616-C620.
- Rane, N., Zou, H., Buelna, G., Lin, J.Y.S. 2005. Sol-gel synthesis and properties of unsupported and supported mesoporous ceria membranes. *J. Membr. Sci.*, 256: 89-97.
- Schutz, R.W. 1993. *Environment behavior of beta titanium alloys*. Japan International. SAMPE Symposium, p.7.
- Stefanov, P., Atanasova, G., Stoychev, D., Marinova, T.S. 2004. Electrochemical deposition of CeO₂ on ZrO₂ and Al₂O₃ thin films formed on stainless steel. *Surf. Coat. Technol.*, 180-181: 446-449.
- Zhitomirsky, I. 2002. Cathodic electrodeposition of ceramic and organoceramic materials. Fundamental aspects. *Adv. Colloid. Interf. Sci.*, 97: 279-317.
- Zhitomirsky, I., Petric, A. 1999. Electrolytic and electrophoretic deposition of CeO₂ films. *J. Materials Letters*, 40: 263-268.
- Zhitomirsky, I., Petric, A. 2000. Electrochemical deposition of yttrium oxide. *J. Mater. Chem.*, 10: 1215-1218.
- Zhitomirsky, I., Petric, A. 2001. Electrolytic deposition of ZrO₂-Y₂O₃ films. *Mater. Lett.*, 50: 189-193.
- Zhou, Y., Switzer, J.A., Allos, J. 1996. Growth of cerium (IV) oxide films by electrochemical generation of base method. *Compd.*, 237(1): 1-5.
- Zufang, Z. 1999. *Corrosion resistance and application of nonferrous metals*. Chemical Industry Press, Beijing, pp.75.