

Cathodic electrosynthesis of alumina thin films and powders

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Formation of ceramic oxide coatings on metallic substrates is a well established technique for protecting metals and alloys against oxidation at high temperature. A wide variety of methods are available for the production of ceramic oxide coatings, namely, plasma spraying, chemical vapor deposition, sputtering etc. [1–4]. These methods, however, suffer from limitations such as high processing temperatures and the difficulty encountered in preparing ceramic oxide deposits with high purity and controlled microstructures. The electrophoretic deposition process [5, 6], using a suspension of the corresponding oxide ceramic powders, involves relatively much less complexity when compared to above processes. However, control of the final microstructure of the coating becomes difficult as it is strongly influenced by the powder characteristics. Recently, formation of ceramic oxide coatings by a sol-gel technique [7–9] has received considerable attention as it offers the advantage of low-temperature processing and the possibility of producing highly pure ceramic oxide deposits with controlled microstructure. However, the sol-gel technique has the limitation of producing the ceramic oxide coatings mostly in the amorphous form rather than the desirable crystalline form.

The electrochemical method of producing ceramic oxide coatings is relatively new, simple and cost-effective. Basically, the metal nitrate is converted into an oxyhydroxide coating over the metal substrate which on subsequent calcination gets converted into the corresponding ceramic oxides. Literature reports reveal that there are two types of electrochemical deposition process, classified, based on the electrode upon which the deposition occurs, as either anodic or cathodic [10–13]. The anodic process, proposed by Tench and Warren [10], is based on the redox change reaction in which a metal is oxidized at the anode by a fixed applied potential. The pH of the solution is adjusted so that although the initial oxidation state is stable, the new oxidation state readily undergoes hydrolysis to form an insoluble metallic oxyhydroxide coating on the anode. The cathodic process, introduced by Switzer [11], involves the electrochemical reduction of water and subsequent deposition of oxyhydroxides on the cathode. Numerous reports are available to date detailing the utility of the anodic process for the formation of simple and mixed oxide films as well as superconductors [14–16]. On the contrary, only a few studies have been reported on the formation of ceramic oxide coatings using the cathodic process [17–24]. However, preparation of

ceramic oxide coatings by a cathodic electrodeposition process presents several advantages over the anodic as well as the alternative coating techniques:

- thickness and morphology of the deposit can be controlled by electrochemical parameters such as electrode potential or current density;
- relatively uniform deposits are obtainable on complex shapes;
- deposition rate is higher than for most other methods; and
- equipment is of low cost

In addition to these processing advantages, the cathodic electrochemical deposition process allows new possibilities in the design of different devices as well as in development of composites. Also, it has aroused considerable interest in the development of nanomodulated ceramic superlattice thin films as such structures are capable of giving superior physical properties [25, 26]. It should be noted that the full potential of this method is only beginning to be recognized. From this point of view its further development, especially on studies related to optimization of the deposition parameters for producing the most common ceramic oxide films having desirable qualities and subsequent extension of this methodology for the deposition of other ceramic materials is of considerable interest. The present investigation is intended to study the utility of cathodic electrosynthesis methodology in the preparation of alumina thin films and powders.

Alumina is an important ceramic oxide material with immense potential for use in an extensive range of engineering products. It is a hard oxide material that possesses excellent resistance to high temperature as well as chemical attack. As result of its characteristic properties, alumina is increasingly finding a place in bearings, valves, pump plungers, engine components, rocket nozzles, shields for guided missiles and vacuum tube envelopes. Alumina coatings are extensively used as thermal barrier coatings, optical wave guides etc.

In the cathodic electrosynthesis of ceramic oxide films, the metal ions present in the solution are atomistically mixed with the hydroxide ions generated at the cathode, leading to the formation of the corresponding metal oxyhydroxide which upon calcination at higher temperatures gets transformed into the corresponding metallic oxide coating. However, attempts made to prepare alumina thin films and powders using aluminum chloride, aluminum sulphate, aluminum nitrate based

electrolytes, at various concentrations of the metal salts and under different operating conditions, did not show similar results. The quantum of alumina thin films and powders prepared from aluminum nitrate solution are high whereas those prepared using aluminum chloride and aluminum sulphate electrolytes are very low. This observation is supported by the fact that during cathodic electrodeposition using aluminum nitrate electrolyte, formation of hydroxide ions following the reduction of nitrate ions is a major contributor to the formation of oxyhydroxide coating on the substrate. Hence, it is evident that the presence of nitrate ions in the electrolyte is highly desirable. However, efforts made to prepare alumina coatings when sodium nitrate is added to an aluminum chloride solution did not produce a satisfactory coating. This may probably be due to the high complexing ability of the chloride ions which effectively binds the aluminum ions, thereby preventing the hydrolysis reaction that leads to the formation of aluminum oxyhydroxide. Hence the use of aluminum nitrate as the precursor electrolyte for the synthesis of alumina thin films and powders seems appropriate. Also, literature reports suggest the use of ammonium nitrate as the supporting electrolyte along with the precursor electrolyte solution for preparing ceramic oxide coatings as well as superconducting films [12, 13, 23]. Hence, it was decided to use 0.1 M aluminum nitrate/0.1 M ammonium nitrate as the electrolyte solution for the cathodic electrochemical deposition of alumina coatings. However, for the electrosynthesis of alumina powders, 0.1 M aluminum nitrate solution by itself was employed.

During optimization of the electrolyte solution, platinum and aluminum were used as anode and cathode, respectively. An attempt was made to look into the possibility of producing alumina coatings on different substrate materials. Among the various substrate materials evaluated, platinum, copper, brass, nickel coated copper and steel exhibit uneven coverage and poor adhesion. The alumina coatings formed on stainless steel exhibit good coverage; but require improvement in adhesion. Aluminum seems to be a better material with regard to both coverage and adhesion of alumina coatings over it. However, aluminum cannot be heat treated at much higher temperatures. In addition, preliminary experiments were also made on the formation of alumina coatings over non-metallic substrates, such as ceramic substrates. Since the ceramic materials are either poor or non-conductors of electricity, there was a surge in the cell voltage, followed by heating up of both the cathode and the electrolyte solution which was found to be detrimental to the formation of the deposit. The only alternative identified was to change the medium from aqueous to either non-aqueous or mixed solvent. For the present study, aluminum and stainless steel substrates are used as cathode materials and platinum serves as the anode.

The applied current density is a major factor in the cathodic generation of hydroxide ions which upon atomic level mixing with the aluminum ions, present in the electrolyte, leads to the deposition of aluminum oxyhydroxide coatings on the cathode. Since the amount

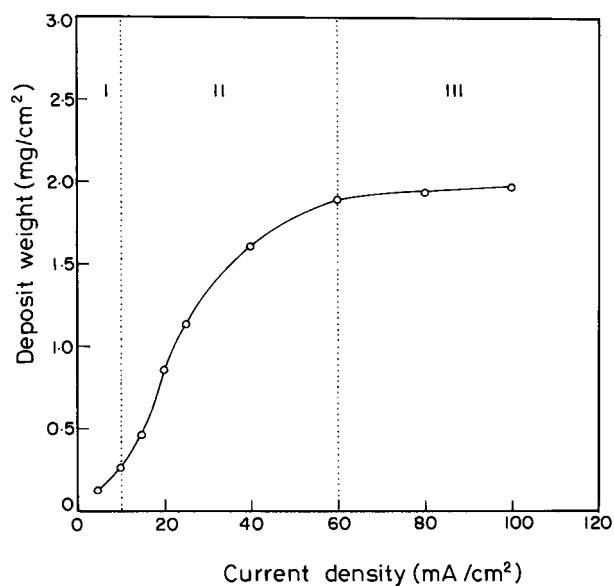


Figure 1 The effect of applied current density on the deposited weight of aluminum oxyhydroxide obtained in a duration of 10 min.

of hydroxide ions generated is a function of applied current density, optimization of this parameter is of paramount importance. In the present investigation, the applied current density values were varied from 5 mA/cm² to 100 mA/cm². Fig. 1 shows the relation between the applied current density and the deposit weight of aluminum oxyhydroxide formed during a period of 10 min. The curve can be divided into three segments based on the applied current density, viz., region I for current densities less than 10 mA/cm²; region II for current densities in between 10 and 60 mA/cm²; and region III for current densities above 60 mA/cm². It is believed that in region I, the only possible reactant leading to the cathodic formation of hydroxide ions is the dissolved oxygen. Since the dissolved oxygen content is very low in the electrolyte medium used for deposition, there is no significant increase in the resultant deposit weight, under a current density of 10 mA/cm². In region II, however, the deposit weight increases linearly with increase in current density. The linear increase is due to the formation of additional hydroxide ions following the cathodic reduction of nitrate ions which increases with an increase in current density in this region. If it is so, obviously, one would expect the deposit weight will be more at high applied current densities. However, the deposit weight obtained above a current density of 60 mA/cm², as shown in region III, did not increase; but rather tended to saturate. From visible observations made during the deposition process, it appears that a greater amount of aluminum oxyhydroxide is forming on the cathode. But, at these current densities, the other possible cathodic reaction is the reduction of water leading to hydrogen evolution. When hydrogen gas escapes from the cathodic surface, it disturbs the oxyhydroxide coating, resulting in spallation of the deposit. As a result the expected increase in deposit weight is not observed.

As pointed out earlier, during the formation of the aluminum oxyhydroxide deposit, because of its poor conducting nature, a surge in the cell voltage is noticed.

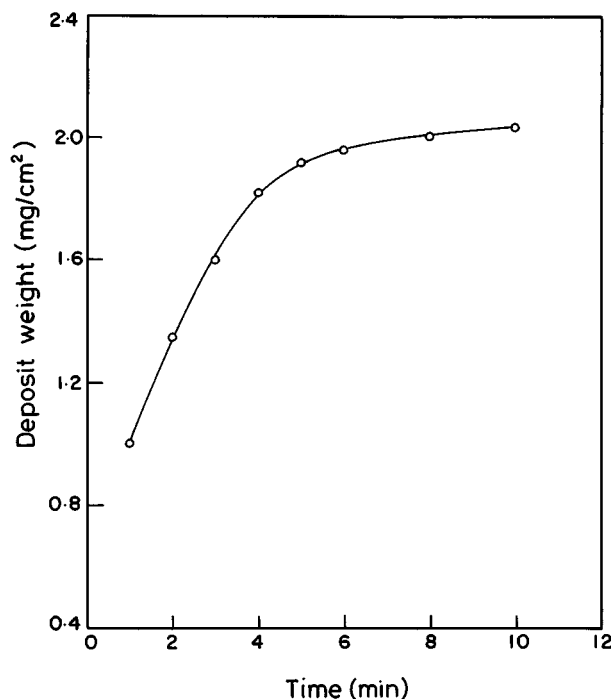


Figure 2 The effect of deposition time on the deposited weight of aluminum oxyhydroxide obtained at a current density of 60 mA/cm².

The increase in cell voltage causes an increase in temperature of both the cathode and the electrolyte solution. Such a condition would cause the diffusion of hydroxide ions away from the cathode, leading to a decrease in the deposit weight. Hence, it is preferable to have proper cooling arrangements or to perform the experiment at lower temperatures of the order of 10 °C.

As the deposit weight increases linearly with the current density only in region II, further experiments were carried out in this region for different intervals of time. Fig. 2 shows the effect of time on the deposit weight obtained at a current density of 60 mA/cm². It is evident from Fig. 2 that the deposit weight started to decrease after 5 min. Although the generation of hydroxide ions, which are the species responsible for formation of coating, is continued for the entire duration of study, the increase in deposit weight is observed only during the first five min. Visual examination at this stage reveals spallation of the deposits after 5 min which resulted in decreased deposit weight.

Based on the effect of process variables and conditions on the formation of aluminum oxyhydroxide coatings, the optimum conditions recommended are as follows:

Electrolyte solution	: 0.1 M aluminum nitrate/ 0.1 M ammonium nitrate
Cathode	: Aluminum or stainless steel
Anode	: Platinum
Current density	: 60 mA/cm ²
Temperature	: 10 °C
Time	: 5 min

The as-deposited aluminum oxyhydroxide coatings are examined visually immediately after the deposition process for coverage and adhesion and for shrinkage after drying. The coverage and adhesion of the aluminum

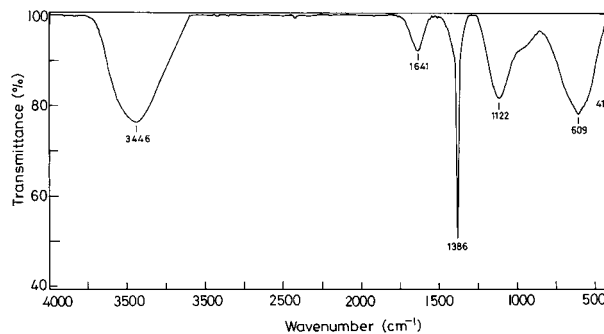


Figure 3 FTIR spectra of the as-prepared aluminum oxyhydroxide.

oxyhydroxide coating are good over an aluminum substrate while on stainless steel the adhesion needs some improvement.

For identifying the phases present in the deposit, the deposits were removed from the substrates and subjected to X-ray diffraction measurements (Shimadzu) using Cu K α radiation. The XRD pattern reveals that the as-deposited aluminum oxyhydroxide deposit is amorphous in nature. The FTIR spectra taken using the same powder (Fig. 3) exhibit the presence of a broad peak at 3446 cm⁻¹ which can be attributed to the -OH stretching mode. The peak at 1641 cm⁻¹ is due to the -OH bending mode of the water molecules. The broad peak at 1122 cm⁻¹ may possibly be due to γ -Al-OH mode and the bands at 417 cm⁻¹ and 609 cm⁻¹ can be assigned to γ -Al-O-Al. Similar assignments were also made earlier by Colomban [27] and Ue *et al.* [28]. The presence of hydroxyl groups as evident from the FTIR spectra supports the fact that the as-prepared aluminum oxyhydroxide powder is amorphous. However, when calcined in a tubular furnace, the aluminum oxyhydroxide powder gets converted to the oxide form and attains the stable α -alumina phase after heat treatment at a temperature of 1200 °C for 2 h (Fig. 4).

As pointed out earlier, **spalling of the oxyhydroxide deposit noted at higher current densities is used as the method to synthesize alumina powders.** It is observed that under optimized conditions it is possible to synthesize alumina powders even in the size of a few nanometers. However, since the experimental procedure involves the application of a much higher current density, it suffers from the problem of **heating up of the electrolyte solution leading to a decrease in the process**

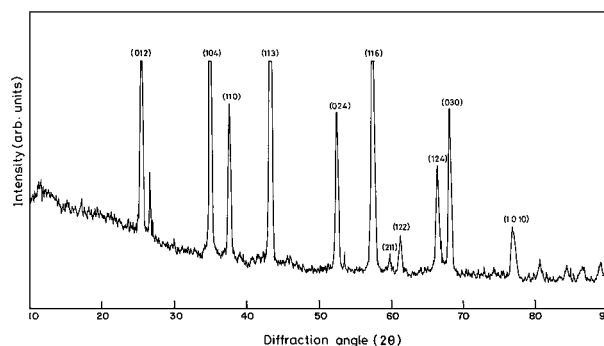


Figure 4 XRD pattern of aluminum oxyhydroxide calcined at 1200 °C for 2 h.

efficiency and yield of the powders. Besides, the change in electrolyte temperature during synthesis might cause a variation in the particle size of the powders. This situation warrants a proper cooling arrangement so as to control the electrolyte temperature. The commercial exploitation of this methodology for the synthesis of alumina powders needs further optimization.

Electrochemical deposition of alumina coatings were successfully carried out, using 0.1 M aluminum nitrate/0.1 M ammonium nitrate solution kept at 10 °C, on aluminum and stainless steel substrates, at a current density of 60 mA/cm² in about 5 min. The as-deposited aluminum oxyhydroxide coating was found to be amorphous in nature. However, after heat treatment at 1200 °C for 2 h, the amorphous aluminum oxyhydroxide phase gets converted to more stable α -alumina phase. The weight of deposit that can be obtained under optimized conditions is limited to only 2 mg/cm². The electrochemical synthesis of alumina powders can be accomplished using a higher current density. However, conditions need to be optimized to achieve increased yield and control of particle size and shape.

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References

1. T. E. SCHMID and R. Y. HECHT, *Ceram. Eng. Sci. Proc.* **9** (1988) 1089.
2. A. HOBAYASHI, N. HESAGAWA and H. NAMIKAWA, *Trans. J.W.R.I.* **18** (1989) 13.
3. C. R. AITA, *Mat. Sci. Tech.* **8** (1992) 666.
4. N. K. HAUNG, H. KHEYRANDISH and J. S. COLLIGON, *Phys. Stat. Sol.(A)* **132** (1992) 405.

5. G. E. F. BREWER, *Am. Ceram. Soc. Bull.* **51** (1972) 216.
6. D. R. BROWN and F. W. SALT, *J. Appl. Chem.* **15** (1965) 40.
7. D. E. CLARK, W. J. DALZELL and D. C. FOLZ, *Ceram. Eng. Sci. Proc.* **9** (1988) 1111.
8. M. SHANE and M. L. MECARTNEY, *J. Mater. Sci.* **25** (1990) 1537.
9. G. R. LEE and J. A. CRAYSTON, *Adv. Mater.* **5** (1993) 434.
10. D. TENCH and L. F. WARREN, *J. Electrochem. Soc.* **130** (1983) 869.
11. J. A. SWITZER, *Am. Ceram. Soc. Bull.* **66** (1987) 1521.
12. Y. ZHOU, R. J. PHILLIPS and J. A. SWITZER, *J. Am. Ceram. Soc.* **78** (1995) 981.
13. Y. ZHOU and J. A. SWITZER, *J. Alloys and Compounds* **237** (1996) 1.
14. M. SAKAI, T. SEKINE and Y. YAMAZAKI, *J. Electrochem. Soc.* **130** (1983) 1631.
15. J. C. G. THOMAS and D. W. WABNER, *J. Electroanal. Chem.* **182** (1985) 25.
16. P. SLEZAK and A. WIECKOWSKI, *J. Electrochem. Soc.* **138** (1991) 1039.
17. L. GAL-OR, I. SILBERMAN and R. CHAIM, *ibid.* **138** (1991) 1939.
18. Y. MATSUMOTO, H. ADACHI and J. HOMBO, *J. Am. Ceram. Soc.* **76** (1993) 769.
19. H. KONNO, M. TOKITA, A. FURUSAKI and R. FURUICHI, *Electrochim Acta* **37** (1994) 2421.
20. I. ZHITOMIRSKY and L. GAL-OR, *J. European Ceram. Soc.* **16** (1996) 819.
21. C. NATARAJAN and G. NOGAMI, *J. Electrochem. Soc.* **143** (1996) 1547.
22. L. ARIES, L. ALBERICH, J. ROY and J. SOTOUL, *Electrochim Acta* **41** (1996) 2799.
23. R. JANES, P. M. S. MONK, R. D. PARTRIDGE and S. B. HALL, *J. Mater. Chem.* **6** (1996) 183.
24. S. K. YEN, *J. Electrochem. Soc.* **146** (1999) 1392.
25. J. A. SWITZER, M. J. SHANE and R. J. PHILLIPS, *Science* **247** (1990) 444.
26. J. A. SWITZER, *Nanostruct. Mater.* **1** (1992) 43.
27. PH. COLOMBAN, *J. Mater. Sci.* **24** (1989) 3002.
28. M. UE, F. MIZUTANI, S. TAKEUCHI and N. SATO, *J. Electrochem. Soc.* **144**(11) (1997) 3743.

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