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Electrodeposition of ceramic films from non-aqueous and mixed solutions

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The preparation of films of TiO_2, ZrO_2 and $PbZrO_3$ by electrodeposition from *N,N*-dimethylformamide solution, has been performed. A new method of cathodic electrodeposition of ceramic films via peroxoprecursors has been proposed and demonstrated on the deposition of TiO_2. The effect of thermal treatment on the phase content of the obtained films and the influence of the solvent used on the deposition process and film morphology were studied.

1. Introduction

During recent years, interest has been generated in electrodeposition of ceramic films [1–9]. Electrodeposition offers advantages such as rigid control of film thickness, uniformity and deposition rate. The method offers the added attraction of simple and low-cost equipment, and the possibility of film formation on substrates of complicated shapes. Undoubtedly, in addition to processing advantages [3–9], this method allows new possibilities in design of different devices as well as in composite development. Electrodeposition has aroused considerable interest for the development of nanomodulated ceramic superlattice thin films [10–13]. Such structures resulted in superior physical properties. 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 and extension to deposition of additional important ceramic materials is of considerable interest.

In this paper we report our results on the electrodeposition of TiO_2, ZrO_2 and $PbZrO_3$ films from dimethylformamide solutions. Titania and zirconia are ceramic materials, extensively used in industry. $PbZrO_3$ belongs to the ferroelectric type materials and is an important component of PZT solid solutions.

2. Experimental procedure

As starting materials, commercially guaranteed salts of $TiCl_4$, $ZrO(NO_3)_2 \cdot nH_2O$, $Pb(NO_3)_2$ and hydrogen peroxide, H_2O_2 (30 wt % solution in water) were used. Electrodeposition has been performed from *N,N*-dimethylformamide (DMF) solutions. The electrolyte concentration was varied from 0.005–0.07 M. Graphite specimens 2 mm × 10 mm × 20 mm were used as substrates. Two counter anodes made of platinum were used. Deposits were obtained at constant current densities ranging from 5–40 mA cm^{-2}. Deposition times were in the range of 1–20 min. After drying at room temperature, the as-deposited films were annealed in air at various temperatures.

The microstructure of the obtained films was studied using scanning electron microscopy (Jeol, Model JSM-840). The phase content was determined by X-ray diffraction with a diffractometer (Philips Model PW-1820), using monochromatized CuK_α radiation at a scanning speed of 0.4° min^{-1}.

3. Results and discussion

Experiments performed with $TiCl_4$ solutions in DMF have not revealed film formation. However, after the addition of hydrogen peroxide to the $TiCl_4$ solution in a molar ratio of 1:1, cathodic deposits have been obtained.

As-prepared films were found to be amorphous, as indicated by the absence of any well-defined diffraction peaks in the XRD patterns apart from peaks of the substrate. Thermal treatment resulted in film crystallization. A typical example of an XRD pattern is shown in Fig. 1. Experimental conditions for film preparation and thermal treatment conditions are designated by the notations in the figure caption. XRD studies revealed the formation of TiO_2 films. As can be seen in Fig. 1, after annealing at 600 °C, peaks of an anatase structure were observed. Thermal treatment in air at higher temperatures results in burning out of the substrate. The main phase content of the powder obtained after annealing at 1000 °C was found to be rutile. In addition to peaks of rutile, small peaks were observed in the X-ray diffraction pattern, which can be attributed to partially reduced titania. The relative intensity of

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† Deceased

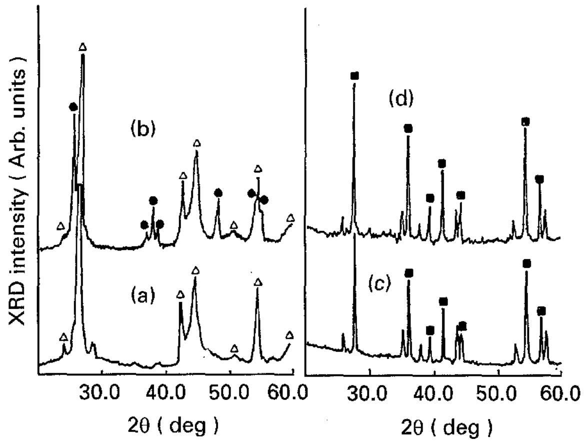

Figure 1 X-ray diffraction patterns of the deposit obtained from a 0.02 M $TiCl_4$ solution in DMF at a current density of 5 mA cm^{-2} (molar ratio $TiCl_4:H_2O_2 = 1:1$). (a) Green deposit; (b) after thermal treatment at 600 °C for 1 h; (c, d) after thermal treatment for 1 h at 1000 and 1200 °C, respectively, and burning out of the substrate. (△) Graphite substrate, (●) anatase, (■) rutile.

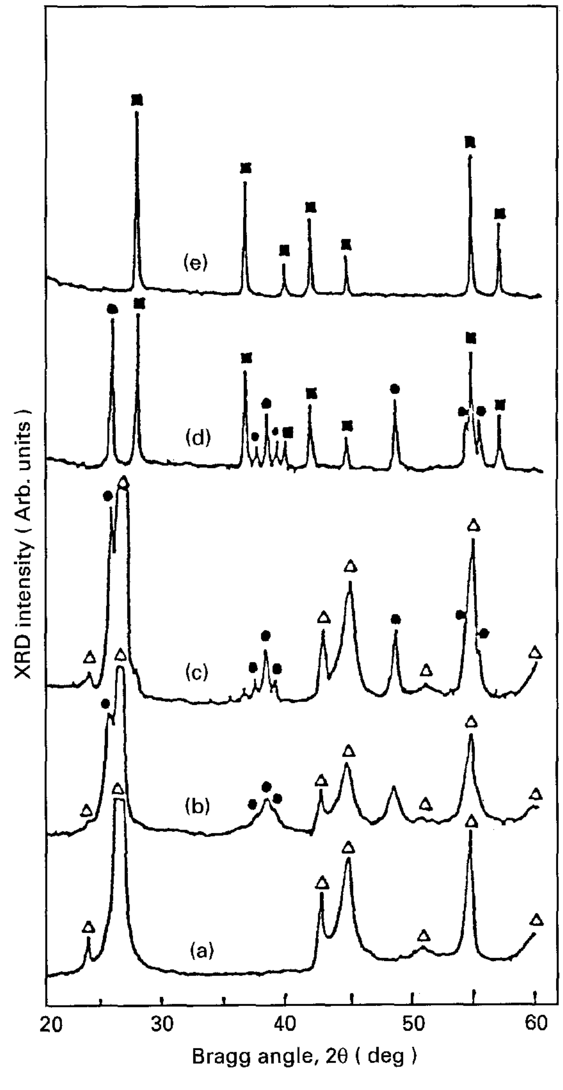

Figure 2 X-ray diffraction patterns of the deposit obtained from a 0.005 M $TiCl_4$ solution in mixed solvent, 75 vol % DMF and 25 vol % H_2O (molar ratio $TiCl_4:H_2O_2 = 1:1$). (a) Green deposit; (b, c, d, e) after thermal treatment at 400, 600, 800, 1000 °C for 1 h, respectively, (d, e) substrate was burnt out. (△) Graphite substrate, (●) anatase, (■) rutile.

these peaks was found to decrease with increase of the annealing temperature.

In order to obtain films of pure titania, experiments have been performed in mixed 75% DMF–25% deionized H_2O solutions (volume contents) with addition of the same amounts of H_2O_2. The phase evolution of the obtained films after thermal treatments at different temperatures is shown in Fig. 2. As-prepared films were found to be amorphous. After thermal treatment at 400 and 600 °C for 1 h, the X-ray diffraction patterns indicate the presence of the anatase phase. At 800 °C, peaks of a rutile modification can be seen and at 1000 °C the X-ray diffraction pattern shows only peaks of rutile.

During the deposition process, the cell voltage was found to increase as shown in Fig. 3. This voltage behaviour is attributed to the increase of deposit resistivity with time. Deposition at higher current densities needs higher voltages. Deposit weight was found to increase with increase of deposition time (Fig. 4) and current density (Fig. 5). Higher current densities and deposition times result in sedimentation of the deposit within the electrolytic bath.

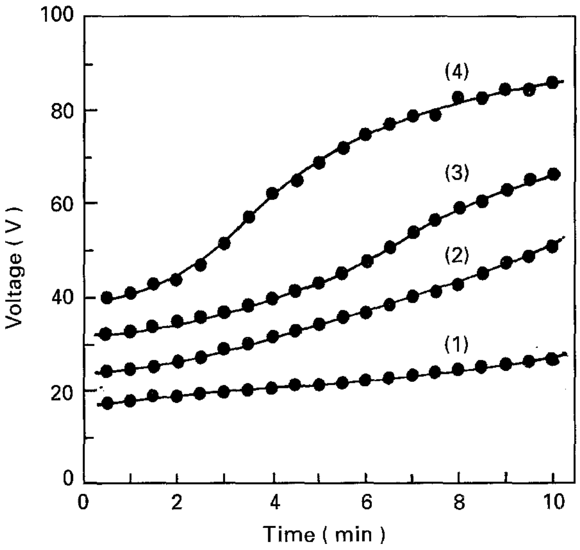

Figure 3 Cell voltage versus time at current densities of (1) 10, (2) 15, (3) 25, (4) 40 mA cm^{-2} (solution composition is the same as in Fig. 2).

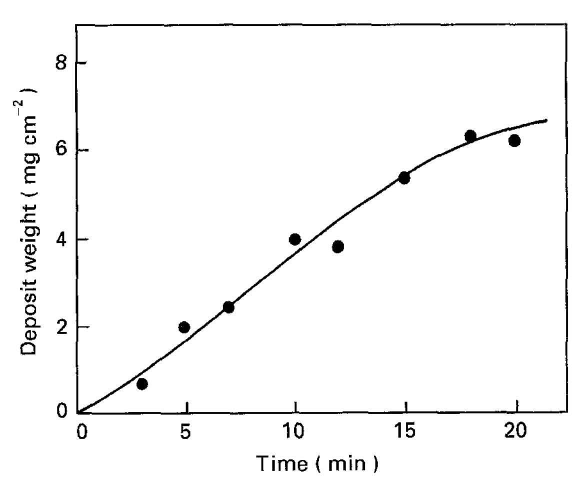

Figure 4 Deposit weight versus time at a current density of 25 mA cm^{-2} (solution composition is the same as in Fig. 2).

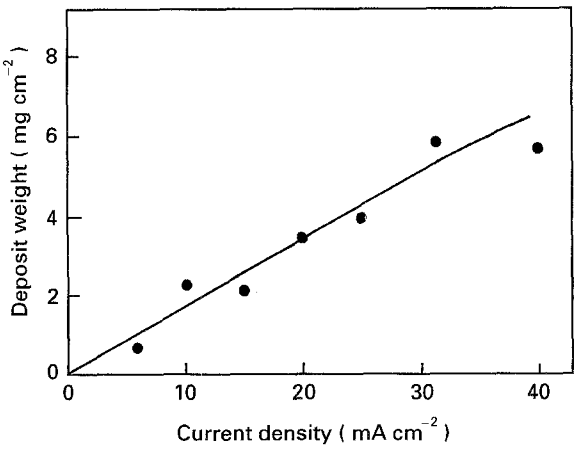

Figure 5 Deposit weight versus current density for a deposition time of 10 min (solution composition is the same as in Fig. 2).

The important point to be discussed is the electrochemical mechanism of film formation. The method of cathodic electrodeposition is based on hydrolysis of metal ions or complexes [4] by the base electrogenerated at the cathode. Different chemical reactions are available for the generation of base: reduction of water, nitrate and organic molecules. Examples of reactions for generation of OH^- in aqueous and non-aqueous solutions were discussed elsewhere [4, 5, 9, 14].

In previous work on deposition of ZrO_2 and Al_2O_3 [5, 15] nitrate salts were used. However, the titanium nitrate salt is not a stable compound and is not available commercially. Difficulties are also associated with the use of $TiCl_4$ in aqueous solutions because the titanium chloride is easily hydrolysed in water. For these reasons, the use of non-aqueous solutions was attempted. However, in pure non-aqueous solutions such as DMF, no deposits were obtained, as mentioned earlier, probably due to lack of cathodic reactants such as H_2O and NO_3^- ions.

In this work we have proposed a peroxide precursor method for titania film formation.

It is now well established [16, 17] that in the presence of hydrogen peroxide, titanium forms a peroxo complex. A hydrolysis reaction provided by the addition of alkali results in the formation of hydrated peroxide. Thermal decomposition of the hydroxoperoxo compound, in turn, leads to the formation of oxide.

We have supposed that a peroxo complex of titanium can be hydrolysed also by the base electrogenerated at the cathode. Our approach to electrodeposition of TiO_2 films is based on hydrolysis of a peroxo complex at the cathode and subsequent thermal decomposition of the obtained hydrated peroxide. By this way the hydrated peroxide films can be considered as a precursor for preparation of corresponding oxide films.

It is important to note that the use of a peroxo complex of titanium allows the problem of instability of titanium salts to be solved and water as solvent can be used.

The sequence of reactions for the formation of TiO_2 films is expected to be as follows.

1. Dissociation of the salt

$$TiCl_4 \rightarrow Ti^{4+} + 4Cl^- \qquad (1)$$

2. Formation of a peroxo complex

$$Ti^{4+} + H_2O_2 + (n-2)H_2O \rightarrow [Ti(O_2)(OH)_{n-2}]^{(4-n)+} + nH^+ \qquad (2)$$

3. Hydrolysis of the complex by the electrogenerated OH^-

$$[Ti(O_2)(OH)_{n-2}]^{(4-n)+} + mOH^- + kH_2O \rightarrow TiO_3(H_2O)_x \qquad (3)$$

4. Decomposition of peroxotitanium hydrate

$$2TiO_3(H_2O)_x \rightarrow 2TiO_2 + O_2 + 2xH_2O \qquad (4)$$

Results of X-ray studies of the crystallization behaviour of TiO_2 films prepared from mixed solutions are in good agreement with the proposed model. It is important to see that the formation of TiO_2 films via a peroxoprecursor needs a certain amount of water. Indeed, experiments with DMF solutions without the addition of water, except the water from the H_2O_2 solution, did not result in pure TiO_2 films.

In experiments with $ZrO(NO_3)_2 \cdot nH_2O$ solutions in DMF, only the formation of a zirconia film was observed. The crystalline structure of the deposit depends upon the annealing temperature. Evidence of crystallinity was observed at temperatures exceeding 350 °C. After thermal treatment at 400 °C, the film consisted of a tetragonal phase. The increase in annealing temperature brings about a transformation from a tetragonal to a monoclinic phase. Fig. 6 shows the X-ray diffraction pattern of the zirconia film after thermal treatment at 600 °C for 1 h. Peaks of monoclinic and tetragonal zirconia can be observed.

The results of the present study as well as those of Abolmaali *et al.* [14] show the feasibility of the

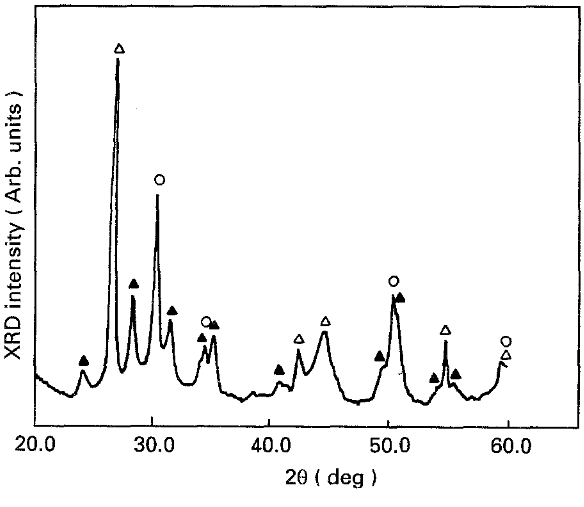

Figure 6 X-ray diffraction pattern of the deposit obtained from a 0.05 M $ZrO(NO_3)_2 \cdot nH_2O$ solution in DMF at a current density of 5 mA cm^{-2} after thermal treatment at 600 °C for 1 h. (△) Graphite substrate, (○) ZrO_2 tetragonal, (▲) ZrO_2 monoclinic.

electrodeposition of ceramic films from non-aqueous solutions. As will be discussed below, the use of non-aqueous solvents has some beneficial effects on the film morphology. It is important to note that experimental conditions for deposition of zirconia from DMF are different from those needed for the deposition of titania from $TiCl_4$ solutions in DMF. In the first case, the solution contains nitrate ions and hydration water of the zirconium salt which are reduced at the cathode. Moreover, the zirconyl ion, in contrast to Ti^{4+}, includes one atom of oxygen. The sequence of reactions for the zirconia film formation in our experiments is supposed to be the same, as described in recent publications [5]. The phase evolution of prepared films after thermal treatment at different temperatures was also found to be similar.

Only limited information is available in the literature on peroxo complexes of zirconium. However, it is known that the hydrated zirconium peroxide can be precipitated from zirconium solutions containing hydrogen peroxide [18]. With this fact in mind we have supposed that zirconium oxide films can be deposited via a peroxo precursor in the same manner as titania films.

We have performed deposition experiments from $ZrO(NO_3)_2 \cdot nH_2O$ solutions in DMF with the addition of hydrogen peroxide in a molar ratio of 1:1. Amorphous deposits have been obtained. Thermal treatment resulted in the formation of zirconia films.

With the experimental techniques used in this work we were not able to find any conspicuous differences in properties of the obtained films as compared to properties of those obtained in experiments without the use of H_2O_2. There are several possible reasons for this, and the observed instability of hydrated zirconium peroxide [18] is one of them. Although we have found no evidence of non-stoichiometry of ZrO_2 films, prepared in our experiments from DMF solutions, this question remains open and additional experiments are necessary in order to study oxygen stoichiometry of ZrO_2 prepared by this way. On the other hand, the use of a mixed solution or thermal treatment of the films in an oxygen atmosphere allow, in principle, possible problems to be solved.

It should be noted that the peroxide route has gained importance in the preparation of fine powders of titanates, niobates and zirconates [17–22], which constitute the most important families of ferroelectric and related materials used in industrial production. This method, which makes use of complex peroxo precursors, enables mixing of the individual components to be achieved on a molecular level, provides the same hydrolysis rate of different components and, as a result, offers strict control over stoichiometry. Individual compounds as well as solid solutions of exact stoichiometry and of very small particle sizes were obtained at relatively low temperatures. In this work we have shown the feasibility of electrodeposition of ceramic films via a peroxo precursor. It should be noted that similar chemical reactions underlie the formation of powders, precipitated by the addition of alkali to a solution containing peroxo complexes, and the formation of a deposit from the same solution by the use of an electrogenerated base.

In the light of the results obtained, it is possible to suggest that different chemical compounds and solid solutions can also be deposited by the use of corresponding peroxo complexes. This approach, in principle, will allow prevention of a serious problem of control of the chemical composition of the deposit.

Recently we have proved the feasibility of electrodeposition of a $TiZrO_4$ double oxide of exact stoichiometry via the peroxide route. This way is analogous to that used [17] for $TiZrO_4$ powder preparation by hydrolysis of titanium and zirconium salts solutions containing hydrogen peroxide. The results of this research will be submitted for publication in the near future.

For the preparation of $PbZrO_3$ films, $Pb(NO_3)_2$ and $ZrO(NO_3)_2 \cdot nH_2O$ solutions were used in a molar ratio of Pb/Zr = 1. XRD studies revealed the formation of $PbZrO_3$ (Fig. 7) after annealing of the obtained films at temperatures above 600 °C. The observed peaks correlated closely with JCPDS data for $PbZrO_3$. The content of undesirable phases was found to be very small. It should be noted that formation of the perovskite $PbZrO_3$ phase was observed at relatively low temperatures compared to temperatures of $PbZrO_3$ formation by the sol–gel technology.

The sequence of reactions leading to the complex $PbZrO_3$ oxide formation is expected to be the following.

1. Dissociation of the salts

$$Pb(NO_3)_2 \rightarrow Pb^{2+} + 2NO_3^- \qquad (5)$$

$$ZrO(NO_3)_2 \cdot nH_2O \rightarrow ZrO^{2+} + 2NO_3^{2-} + nH_2O \qquad (6)$$

2. Hydrolysis of the zirconyl ion

$$ZrO^{2+} + H_2O \rightarrow Zr(OH)_2^{2+} \qquad (7)$$

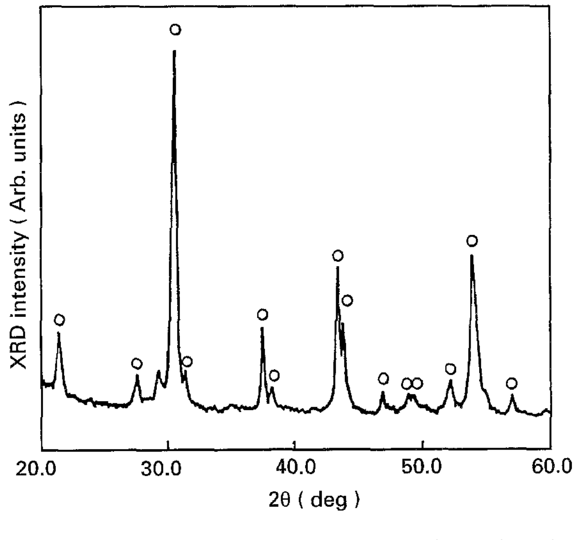

Figure 7 X-ray diffraction pattern of the deposit obtained from a mixed 0.02 M $ZrO(NO_3)_2 \cdot nH_2O$ and 0.02 M $Pb(NO_3)_2$ solution at a current density of 20 mA cm^{-2} after thermal treatment at 650 °C for 6 h (under these conditions the substrate was burnt out). (○) $PbZrO_3$.

3. Interaction with OH^- ions

$$Pb^{2+} + 2OH^- \rightarrow Pb(OH)_2 \quad (8)$$

$$Zr(OH)_2^{2+} + 2OH^- \rightarrow Zr(OH)_4 \quad (9)$$

4. Dehydration and formation of a complex oxide

$$Pb(OH)_2 + Zr(OH)_4 \rightarrow PbZrO_3 + 3H_2O \quad (10)$$

Attempts were also made to prepare $PbZrO_3$ from aqueous solutions. The deposition rate of lead was found to be much higher than that of zirconium. The Pb/Zr atomic ratio in solution was varied from 0.4–1.0. In all cases, an undesirable phase content in the deposit was comparable to the content of the perovskite phase. Initial pH adjustment provided only a slight increase in the yield of the perovskite phase.

Electron microscopy studies have shown that the morphology of the obtained films was distinctively different from that of the films prepared in aqueous solutions. As an example, Figs 8 and 9 show scanning electron micrographs of the surface of the dried green films prepared from $TiCl_4$ and mixed $ZrO(NO_3)_2 \cdot nH_2O$ and $Pb(NO_3)_2$ solutions. It should be noted that the microstructure evolved in aqueous solutions frequently shows a flaky shape of the particles [8] and aggregates [5]. Dendritic morphology of the deposit was observed in our attempts at electrodeposition of $PbZrO_3$ from aqueous solutions. In contrast, films prepared from DMF solutions in the present study have shown more uniform, dense, and continuous microstructures. However, further optimization of the drying process is needed in order to prevent crack formation.

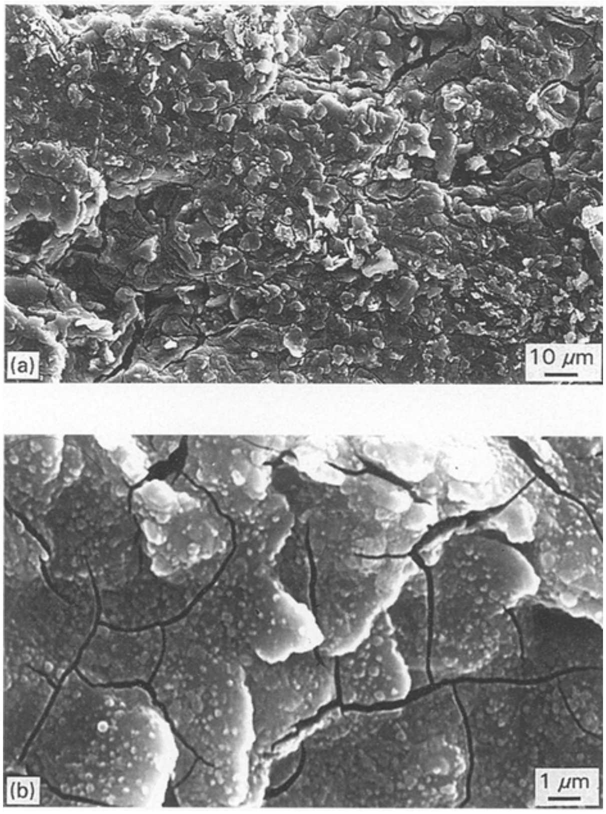

Figure 8 (*a, b*) Scanning electron micrographs at different magnifications of the green deposit obtained from a 0.02 M $TiCl_4$ solution in DMF ($TiCl_4$:H_2O_2 molar ratio = 1:1) at a current density of 20 mA cm^{-2}.

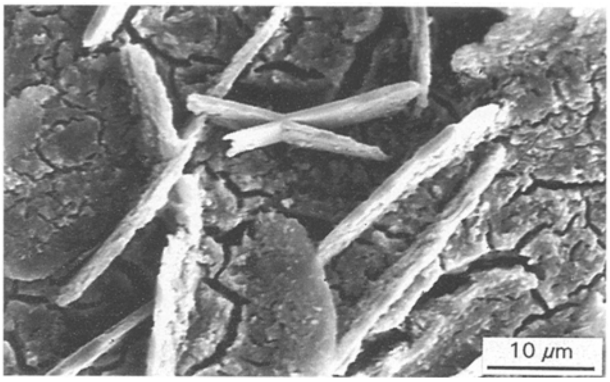

Figure 9 Scanning electron micrograph of the green deposit, obtained from a 0.02 M $ZrO(NO_3)_2 \cdot nH_2O$ and 0.02 M $Pb(NO_3)_2$ solution in DMF at a current density of 20 mA cm^{-2}.

Inorganic solvents are now successfully used for agglomerate-free processing of ceramic powders by wet chemical methods. The use of non-aqueous solvents allows adsorbed water to be removed and, as a result, prevents the formation of agglomerates and aggregates. The adsorbed water in green films also leads to cementation of small particles to form aggregates and diminishes the advantage of the electrodeposition in producing films with nanosized particles. Hence, the use of non-aqueous solutions should eliminate this problem. Non-aqueous solutions allow electrochemical water decomposition to be avoided [14], and therefore the porosity of films, resulting from gas bubbles formed during this process, is prevented.

4. Conclusion

Experiments were carried out on cathodic electrodeposition of TiO_2, ZrO_2 and $PbZrO_3$ films from DMF solutions. Results obtained have shown the feasibility of the preparation of zirconia and $PbZrO_3$ films starting from lead nitrate and zirconyl nitrate salts. In order to overcome the problems of electrodeposition of TiO_2 the peroxo precursor method has been proposed. Electrodeposition of TiO_2 has been performed via a peroxo precursor from a mixed DMF–water solution (volume ratio 3:1). The effect of thermal treatment on the crystallization behaviour of the obtained films has been studied and the influence of the solvent used on their morphology has been discussed. The proposed peroxo precursor method allows new possibilities in electrodeposition of ceramic materials and deserves further exploration.

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