

Sol-Gel Processing for Preparation of Metal Oxide Films

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Abstract

Systematic research of metal alkoxide electrophoretic deposition has been developed. The formation mechanism of electrophoretic deposits has been offered. The structure study of dry and heat-treated electrophoretic deposits has been established. The concrete examples of one and bi-component oxide thin film formation were considered. The new approaches for thin film technology have developed on various substrates of different shapes and sizes. The correlation between thin film structure, mechanism of their formation, and physico-chemical properties has been determined.

Introduction

Properties of thin films are generally fixed by the chemical composition and crystalline structure. Synthesis of these materials by chemical polymerization and electrophoretic deposition at low temperatures, on the other hand, permits significant modifications to the ultrastructure. These structural modifications in turn modify the material properties, without compositional alterations. The number of possible precursors, the number of possibilities, and the number of reaction parameters within the different steps lead to an immense number of variables. It means that the chemistry behind this is a very complex one. In addition to this, characterization of reaction mechanisms, intermediates and even polymers becomes difficult, too [1-3]. In this paper, the objectives of investigation are not only the illustrations some special chemical aspects of electrophoretic deposition and metal alkoxides in the producing of thin films from the material science point of view, but also the problems, which arise and which have become clear due to the immense work of numerous scientists on the basis of their competencies and their respective potential.

Our main idea is to understand the microstructure

- processing - property interrelationships with a view towards prediction of oxide systems with good functional properties [4-5].

Experimental part

Electrodeposition of organic coatings has found wide spread industrial application during the past ten years. The rapid world - wide acceptance of electrodeposition - usually called "electrocoating" - is due to many advantages. They are: obtaining an uniform and dense coating, controlling easily the coating thickness by the deposition voltage and deposition time, obtaining various shapes and sizes of coating on various substrates, large saving in cost, when compared with spray or dip coat application. It seems, therefore, desirable to experiment with electrodeposition of metal alkoxides. This technique has the advantages that it is applicable to substrates with large areas and complicated shapes and is relatively simple, and thus low cost.

Chemistry plays an important role for the sol-gel process. It is complex and in most cases it is difficult to evaluate mechanisms. It seems to be very difficult to separate the reactivities of single components, especially with respect to multi-component

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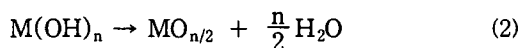
system, but these systems are very often of highly practical interest. The distinction between sols and gels can be summarized as follows: a sol represents a suspension or dispersion of discrete colloidal particles; while a gel represents a colloidal or polymeric solid containing a fluid component. The most obvious features of this reaction, the transition from a liquid (solution or colloidal solution) into a solid (di- or multi-phasic gel) led to the expression "sol-gel process".

The evolution of the sol-gel process took place in three progressive stages:

- Use of colloids and organometallic compounds as starting materials.
- Formation of monolithic materials from gels.
- Modification of material properties by molecular structural variations.

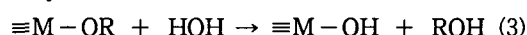
Use of organometallic compounds is relatively recent. The attractive properties of these materials as ceramic or thin film precursors include high purity and reactivity, submicron particle size, capability of producing monosized powders, and use in coating technology. Electrophoretic method makes it possible to coat the substrate at low temperatures, and very large surfaces. It allows maintenance of the monolithicity of larger volumes of gel during the drying and pyrolysis to a pure oxide state. A most recent and significant development in this field has been the ability to affect the substructure of thin films by controlling the kinetics of the chemical reactions that form their network structure. These structural variations alter significantly the behavior of these materials and modify their basic properties.

Metal alkoxides, among the organometallic compounds, are of particular interest to inorganic materials scientists. Alkoxides of almost any metal can be synthesized, and those of group III and IV metals - which encompass a large portion of the glass and ceramic composition - are available commercially at relatively low cost. When brought into contact with water, these materials hydrolyze vigorously, forming metal hydroxide and oxide powders:

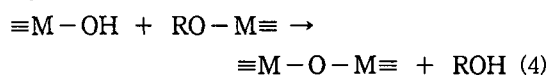


The hydrolysis reaction shown in equation 1, although frequently adequate, is oversimplified. Actually, there are two simultaneous reactions involved in the hydrolysis of metal alkoxides:

Hydrolysis:



Polymerization:



Where M is a metal with (IV) valence, for example. Both reactions between the OH and R groups occur concurrently. The second reaction, however, by creating an oxygen bridge between two metal ions, leads to the formation of an oxide network. Under normal circumstances, the growth of this network is limited.

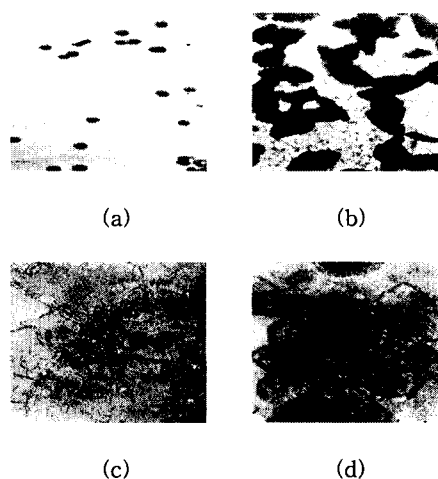


Fig.1. Different forms and size of different metal alkoxide particles: a - BaTi(OR)₆, b - ZrY(OR)₇, c - Al(OR)₃ in fresh sol, d - Al(OR)₃ in aged sol.

In our work the electrophoretic techniques is developed which allowed maintenance of the monolithicity of larger volumes of gel during the

drying and pyrolysis to a pure oxide state. The structural variations alter significantly the behavior of these materials and modify their basic properties. Usually, electrically charged, colloidal dispersed particles are attracted by the electrode of the opposite polarity in an electric circuit. Electrocoating materials will also require other special properties, which are enumerated below. First, the film former must be compounded to form dispersions of macroions from which films can be electrodeposited. Second, these films must volatilize at temperatures below the softening point of the ceramics. Third, the metal alkoxide must cause high electrical resistance during the deposition process. Fourth, the metal alkoxide must be compounded to give a coating bath, which remains stable over long periods of agitation, etc.

The major distinction of the present work lies in the method of accomplishing the hydrolysis reaction. In our case, water is not added to the system. Instead the metal alkoxide complex/alcohol solution is exploited by the electrophoretic deposition in order to prepare thin solid films. Gels prepared by hydrolysis of metal alkoxides during electrophoretic deposition at room temperature and standard atmospheric pressure contain water and alcohol.

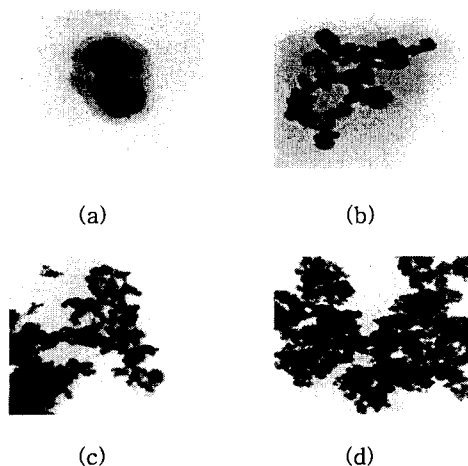


Fig.2. Formation of gel net during electrophoretic deposition of metal alkoxide sol (a-d).

When the gels are heated, they liberate the

(water + alcohol) and convert into the nonporous impervious glasses. Many variables, such as composition of starting materials and low or big moisture content affect the gels produced during the sol-gel transition. The rheological property of a sol may provide information on sol and gel structures. The process of making monolithic thin coating film involves four basic steps: 1) Hydrolysis of alkoxides, 2) Peptization of the hydroxides to a clear sol, 3) Gel formation, 4) Pyrolysis to metal oxide.

The inorganic structure is also modified by the kinetics of the hydrolysis and polymerization reactions, which form the structure. The principle parameters, which affect the kinetics of these reactions are: 1) Selection of starting compounds and host medium, 2) Water/alkoxide ratio, 3) Electrochemical effects, 4) Reaction temperatures.

By electrophoretic deposition the chemical polymerization of the alkoxide systems by external electric field eventually leads to gellation, and the nature of such gels is fundamentally different from that of the gels produced in colloidal systems. In view of the previous results, the proposed research concentrated on the development of such thin films, which have shown promise. Their physical and mechanical properties were measured and other chemical characteristics were determined. A large amount of the work emphasized the effect of the sol-gel parameters, such as age of alkoxides, sols and gels, environment temperature, drying and firing, etc. Study of the reaction products was carried out using electron microscopy, XRD, DTA, IR-spectroscopy and measurement of other chemical and physical characteristics (specific surface, stability, porosity etc.)

Results and Discussion

Despite the important progress in the investigations of the mechanisms of thin film preparation, a direct relation of reaction parameters to material properties is still very difficult. However, if the kinetics of the hydrolysis and polymerization reactions can be controlled, it is possible to form

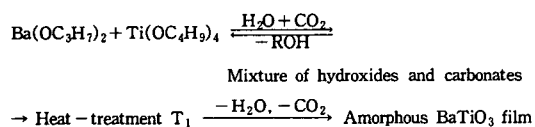
an extended oxide network. This yields a monolithic material in almost all oxide systems.

Once a gel has been formed, it must be dried to remove the solvent phase. The method of drying is influenced by the intended use of the dried material, but is largely independent of the degree of crystallinity or the state of decomposition of the gel. In obtaining monoliths from gels, the drying procedures are largely determined by the need to minimize internal stresses associated with the volume changes on drying and the capillary forces in the gel pores.

If monolithic materials are desired, special care must be taken to ensure complete removal of water, organic groups, or decomposition products, prior to micropore collapse to avoid the development of stresses leading to fragmentation. The nature of the porosity and its evolution with respect to removal of residues plays a key role in determining integrity. For gels made from metal alkoxides with relatively slow rates of hydrolysis and condensation, a considerable number of hydroxyl and organic groups may remain in the gel even after drying.

With non-optimized firing schedules, residual organic groups and H₂O can lead to blackening and fragmentation, as well as to the formation of bloated and foamed samples. Gels produced from the hydrolysis of alkoxides without excess water generally have a high residual organic content upon drying; and their early densification often leads to pore closure and entrapment of residual gases.

The firing of gel monoliths leads to a generalized densification of the structure. The achievement of densification at low temperatures is often limited by the competing process of crystallization (once an initially amorphous sample crystallizes, it can be fired to complete density only at relatively high temperatures). For example,



→ Heat - treatment $T_2 \rightarrow (T_2 > T_1) \rightarrow \text{Crystalline BaTiO}_3 \text{ film}$

Scheme process of crystalline BaTiO₃ film formation

As a result it is proposed to work out the main principles of practical control of the process, structure and phase formation ensuring a given set of physical properties.

- (1) Determination of the kinetics of hydrolysis and condensation, and characterization of the structural state prior to gelation. Characterization of the chemical and physical structure at various stages of reaction prior to gelation, using the full panoply of techniques available to the practicing chemist/physicist. Such activity should begin with a characterization of the state of aggregation on the precursor materials, and be carried through the initially formed structures, to the development of the gel state by the various routes. Investigations of the chemical and physical changes, which take place on aging sols and gels.
- (2) Characterization and optimization of drying procedures. Considerable attention to be directed to the processes, which take place on drying and to an exploration of various approaches to removal of the solvent phase. Included here are the effects of stress relaxation, the development and avoidance of capillary stresses, the effects of pore size and pore size distribution, and particularly the exploration of non-conventional approaches to drying.
- (3) Characterization of the processes, which take place on firing and optimization of firing procedures. As noted above, the firing of a dried gel can be accompanied by a large number of physical and chemical processes. Several of these processes need to be characterized in much better detail, most notably the process of viscous sintering and the competition between sintering and crystallization. With such information, it should be possible to develop processes for the production of thin films with novel properties, produced at exceptionally low temperatures.

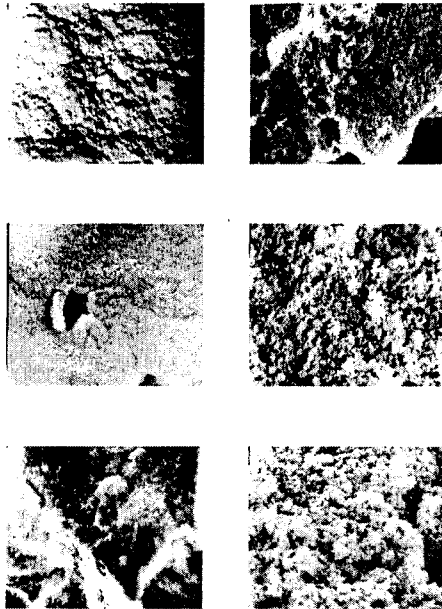


Fig.3. Drying procedure of gel electrophoretic films at different conditions.

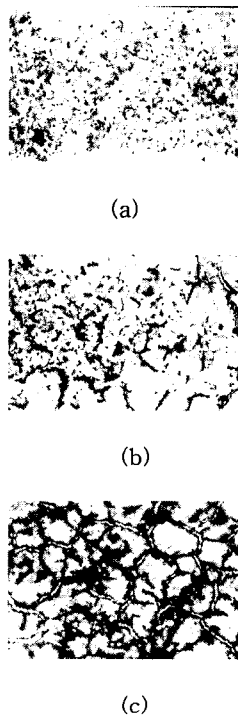


Fig.4. Dense film (a) and crack films (b-c) with different firing procedures.

(4) Formation of complexes and characterization of reaction products in multi - component systems. Since many of the most interesting oxide materials, which can be obtained from gels consist of several chemical components, it is imperative that advantage be taken of complex precursor formation. Exploration of novel applications for electrophoresis-derived thin films (Table).

As noted above, the use of gel techniques offers the opportunity of impacting broadly the science and engineering of thin films materials. The principal issues to be explored here include the development of pinhole-free coatings, and the exploration of mixed-inorganic systems.

Table. Room temperature properties of functional oxide films

	Al ₂ O ₃	Al ₂ O ₃	BaTiO ₃ + La ₂ O ₃	BaTiO ₃ + BaZrO ₃	Y ₂ O ₃	ZrO ₂ + Y ₂ O ₃
Structure	amorphous	amorphous+ δ Al ₂ O ₃	crystal	crystal	crystal	crystal
Thickness, nm	300	500	300	400	300	300
Dielectric constant, f=10 ⁶ Hz	7.2	7.8	90	1000	12	40
Resistivity Ω · cm	6 · 10 ¹³	9 · 10 ¹²	1.7 · 10 ¹³	5 · 10 ¹²	1.8 · 10 ¹³	7 · 10 ¹⁴
Electric strength, 10 ⁶ V/m	4.5	3.9	0.2	0.1	2.1	0.5
Mechanic strength, MPa	24	29	18	25	14	48
Dielectric loss, 10 ⁻⁴	10	15	2.2	1.0	1.0	1.2

Conclusions

1. In the electrophoretic process a metal alkoxide solution is gelled through hydrolysis-polymerization and converted the gel thin layer to an oxide by heating at relatively low temperatures.
2. Detailed investigation of the oxide crystallization process was carried out, and the crystallization conditions and origin of the dielectric properties were discussed.
3. Special attention was paid to the problem of modification of material properties by molecular structural variations.

Acknowledgement

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