

SOL-GEL PROCESSING AND MATERIAL SCIENCE

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Abstract

Sol-gel processing, which started some decades back as a laboratory curiosity, has proved to be a powerful and versatile technique for the synthesis of materials. The utility of the sol-gel method for producing glass and ceramic materials in the form of powders, fibers, thin films and bulk shapes with high purity, functional microstructures and potentially high chemical homogeneity at relatively low temperature (compared to conventional processing) has been discussed.

Introduction

The secret to improving any kind of material is to control its structure at very small length scales in an early stage of fabrication; and chemistry may be the way to achieve this goal. The new materials tend to fall into 2 groups, those of interest for electrical, optical, or magnetic applications and those having outstanding mechanical or structural performance, especially at high temperatures. Sometimes both kind of properties are needed at once.

On top of other virtues, ceramics are less dense than metals, so parts are lighter, and raw materials are abundant. But the main problem was not solved. Ceramics are well known to be brittle; they deform very little before failing catastrophically. While this aspect of brittleness is an unpleasant fact of life, engineers could design parts in such a way as to emphasize the strong points of ceramics, such as strength at high temperature in structural materials, while minimizing this liability. And since every ceramic part has a different distribution of defect, the load that will generate an internal stress exceeding the threshold somewhere in the part cannot be predicted. Ceramists have little control over their starting material.

The hope is to control the structure of features in ceramic materials having characteristic length scales of 10 nanometers and up. The small length scale has given rise to the term ultrastructure processing.

The chemical technique that has attracted the most attention is sol-gel processing. The sol is a suspension of small particles (colloids) ranging in size from about 1 to 100 nanometers. On partial loss of the liquid phase, the sol increases in viscosity, eventually becoming rigid; that is, it becomes a gel. The gel is the starting material for subsequent processing stages in ceramic, glass and thin film fabrication. The hallmarks of the technique are its simplicity and relative inexpensiveness. Nowadays, most sol-gel research also involves metal oxide ceramics made from metal alkoxides.

Experimental

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 are generally porous and contain water and alcohol. When the gels are heated, they liberate the water + alcohol and convert into the nonporous impervious glasses. The coating was carried out in an electrophoresis manner in a humidity-controlled glovebox. The lateral electric field is produced by two graphite

electrodes which were connected to the two poles of a conventional electrophoresis power supply. Gel on the electrode of 1.0 - 1.5 mm thickness electrophoreses for about 1 - 5 min at 500 - 700 V. The pH gradient from 7 to 5 near the electrode position was observed. The quality of the films was very sensitive to the humidity of the atmosphere, as mentioned above.

Transparent films were obtained below 20 % relative humidity at 20 °C. The substrates coated gel were kept for a while in the glovebox to let the solvents evaporate and then heat-treated in air. The temperature of heat treatment was raised stepwise at intervals of 100 °C for 10 min. The thickness of the coating films, as measured by surface profilometer, was in a range of 300 to 500 nm, depending on the mole ratio alkoxides and on the degree of dilution of the coating solution by ROH. The load at scratch was measured on films 60 nm thick; though the IR spectra were measured on films 300 nm thick. Thermogravimetry (TGA) and differential thermal analysis (DTA) were conducted in air at a rate of 10 °C min⁻¹; α - alumina was used as the reference for the DTA. The surfaces of the coating films were observed by scanning electron microscopy (SEM). The shrinkage of the gels on heating was measured by a heating rate of 5 °C/min. The water concentration in the non-porous films prepared by heating the gels was determined by measuring the infrared absorption at 3670 cm⁻¹.

Results and Discussion

Many variables, such as composition of starting materials and low or big water content affect the gels produced during the sol-gel transition. The rheological property of a sol may provide information on sol and gel structures. During electrophoretic deposition viscosity changes near the electrode position.

In the case of electrode gel the results exhibit Newtonian flow behavior and spinnability at viscosities higher than 18 Poise while the "open system" exhibits no spinnability. It has been found that the viscosity of electrode gel and as-prepared "open system" changes against "aging time" of alkoxide complex at 25 °C. The viscosity of "age" alkoxide electrode gel increased rapidly within a short time showing a rapid gelation whereas the "open system" of alkoxides shows much slower gelation. It seems

that long-shaped structures or linear polymers are developed in the pH electrode gradient with a low water content (from air moisture) during electrophoresis of mixed alkoxides. On the other hand the "open system" with the same mole % acid and water does not contain chain-like or one dimensional structured polymers near gelling point. The influence of the following conditions on the quality of the films was studied: (a) concentration of the solution; (b) successive operations of electrophoretic deposition and thermal treatment; (c) the presence of moisture traces in the solution and the "age" of the solution, that is the time passed from its preparation to the moment of utilization. The films were colorless, very adherent, and consisted of grains estimated optically to be below 0.05 and 1.10 μ . Tests were made to determine causes of porosity, to reduce the porosity to a specified value. The shrinkage of significance is that which occurs between gelation of the sols on drying at room temperature and firing above 500 °C. Shrinkage was measured by evaporating, drying, and firing the solution and measuring the volume at each stage. Fresh sols of mixed alkoxides cheated with isopropanol gave a low value of shrinkage of 97 - 98 %. Since an appreciable fraction of the porosity is undoubtedly not interconnected, electrophoresis film procedure would be practical only with much smaller shrinkage systems.

Already, researchers can make ceramics with a wide variety of properties by sol-gel processing, although in almost all cases the economic utility of this approach is still an aspect requiring consideration is one occurrence of electrochemical reactions during electrophoretic deposition. The moderate unanswered question. This paper reported what it is now possible to do with sol-gel processing. Materials processing begins with mixing metal alkoxides, alcohol and sometimes water and a catalyst. Subsequent steps depend on what type of material is to be prepared, but they all take place at much lower temperature than the usual glass or ceramic-forming processes, potentially a considerable economic advantage.

To make light weight, transparent polymer-oxide composites with controllable indices of refraction, for example, the solution is cast in a mold and allowed to gel, which produces a transparent gel comprising a network of particles about 5 nanometers in diameter and

pores between the particles about twice this size. After drying and heat-treatment steps, the porous gel is impregnated with monomers, which subsequently polymerize at room temperature in pores of the gel.

Electrophoretic deposition has received considerable attention over the past 30 years. Effort has tended to be concentrated more on the electrochemical aspects of the process. Sol-gel related aspects during electrophoretic deposition on the other hand, generally have received less attention. These aspects include such topics as the properties of starting powders, the removal of formed sample from electrodes or not without cracking, shrinkage accompanying drying and sintering, effects associated with specific additives and impurities, sintering characteristics of the formed coating, and scale-up problems.

The most common method for charging solid particles for electrophoretic depositions is by adsorption, usually of a proton or other cation. Positively charged particles usually result. The main control problem is the sensitivity of the charging process to the presence of impurities, particularly water which can serve as a proton donor. The adsorption and dissociation modes are in competition. Particle charging, as made evident by electrophoretic deposition rates under certain standardized conditions, is affected by as little as 0.02% to 0.03% water. This fact was established initially by back-addition of water to dried alcohol. One other electrochemical currents from alcohol sol are believed to be mainly of electrochemical rather than of electrophoretic origin. The main concern, however, is with formation of gaseous decomposition products at electrodes. Gas bubbles can knock deposits off electrodes at higher evolution rates and at lower rates can introduce large pores in green coating which are not removed by sintering. So we may say, that an important innovation introduced into electrophoresis was the use of organic liquids in place of water to reduce complications arising from such reactions. Some advantages of forming by electrophoretic deposition were briefly discussed. Since this process involves use of $\approx 0,01 - 0,001\mu\text{m}$ particles and is non-Faradaic, deposition times are short, of the order of a minute, in contrast to those required with conventional electroplating. A number of shapes are formable with simple tooling with the limitation that deposit thicknesses be no greater than $\approx 1\text{mm}$.

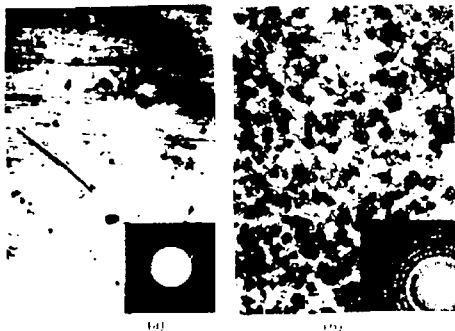
Probably the most attractive feature is the excellent sinterability of green coating. In the course of particle charging, deflocculation occurs and particle agglomerates are broken up. Consequently, the "building block" of the green structure obtained by electrophoretic forming is the ultimate crystallite or, at most, small aggregates of such crystallites. Another advantageous feature of electrophoretic forming relates to dimensional control.

Finally, the cost of forming by electrophoretic deposition was compared a few years ago with isostatic pressing, the most commonly used alternative forming procedure by experienced manufacturing engineers. The costs were nearly the same

We investigated the application of these films to other substrates.

Brilliant transparent and colorless and strongly adherent films were obtained on Pt, Al and stainless steel foils. In the case of Al and stainless steel foils, particularly, it is observed that the color is like gold because of the addition of reflective light from the substrates. Here we may draw the following conclusions.

1. Using a sol-gel process, transparent films of BaTiO_3 were prepared by electrophoretic deposition 300-500 nm in thickness.
2. The coating films using the as-prepared sol appeared more transparent and had stronger dielectric properties compared with the coating obtained from the 24-h sol. Finer texture was observed in the surface of the former by SEM.
3. The electron diffraction analysis showed that the film from "fresh" sol was partially crystallized, and the heat-treated gels from 24-h sol were crystallized more.
4. The amount of air moisture, as well as the "age" and types of alkoxides and solvents and also the electrophoresis conditions should be considered to investigate the structure development during the sol-gel transition.



Transmission electron micrographs and electron diffraction patterns of (a) as-prepared film, (b) gelled and heat-treated solution

Reference

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Table. Room temperature properties of 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, Ohm.cm	6.10 ¹³	9.10 ¹²	1,7.10 ¹³	5.10 ¹²	1,8.10 ¹³	7.10 ¹²
Electric strength, 10 ⁸ V/m	4,5	3,9	0,2	0,1	2,1	0,5
Mechanical strength, Mpa	24	29	18	25	14	48
Dielectric loss, 10 ⁻⁴	10	15	2,2	1,0	1,0	1,2