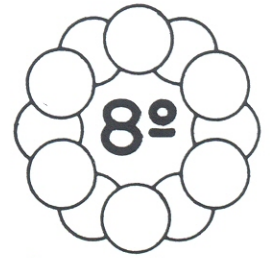




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SOL-GEL TECHNOLOGY: FROM POLYMERS TO ADVANCED CERAMICS AND GLASSES

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SUMMARY

An overview of the critical steps in sol-gel (SG) processing of ceramics and glasses is presented and includes the synthesis, drying and sintering steps, as well as a discussion on the relative merits and disadvantages of the SG technique over more traditional processes. Both present and future applications are described.

INTRODUCTION

The sol-gel (SG) process for making glasses and ceramics is now an intensely studied topic in materials science and engineering. The development of the SG process for scientific studies in ceramics started during the World War II [1] based on the fundamentals of colloid chemistry. Here it is convenient to define two terms: Sols: microscopically (colloidal) homogeneous permanent suspensions of solid particles in a liquid [2]; Gels: solids usually containing a fluid component and having a network internal structure so both the solid and the fluid components are in a highly dispersed state [2].

In the early 60's the interest of colloid chemists began to converge with that of ceramists in the preparation of concentrated sols of many oxides and in their gelation. However, the "explosion" in SG science and technology only took place in the early 1980's simultaneously with the advanced ceramics fever.

The advantages of the SG approach are closely related to the ability to produce: i) powders with a small mean size and a narrow distribution of particle sizes, or monolithic pieces which can be sintered to high density at comparatively low temperatures, ii) powders and bodies with exceptional chemical homogeneity, iii) glasses with novel compositions and combinations of properties, iv) ceramics with novel microstructures, including novel distributions of phases and properties, v) coatings with specified chemistry and desired combinations of properties, vi) shaped bodies and coatings with exceptionally high porosity (specific surface area) and tailored chemistry of the surfaces of the pores, vii) materials combining both organic and inorganic functionality.

The main disadvantages of SG processing are the high cost of the starting materials (alkoxides), the special, and in many instances, difficult processing conditions as well as the severe cracking that very often occurs during elimination of the solvent.

The sol-gel processes of interest can be divided in the following categories [3]: i) Prepare fine, reactive, unagglomerated powders, form green bodies and sinter them to form dense ceramic bodies; ii) Prepare gels by direct polymerization in solutions of hydrolyzed organometallic or metal salt precursors, dry and sinter to obtain ceramic pieces, coatings or fibers; iii) Prepare sols of desired chemistry, convert the sols to gels, dry and sinter to eliminate heteroatoms and porosity; iv) Prepare dispersions of preformed particles synthesized by other methods, effect gelation, and proceed following the general approach of gel to ceramic processes.

Next, an overview will be presented on the critical steps of the sol-gel processing, including drying

and sintering, following by a discussion on both present and future applications.

THE SOL-GEL PROCESS

A schematic diagram of the sol-gel process is depicted in Figure 1.

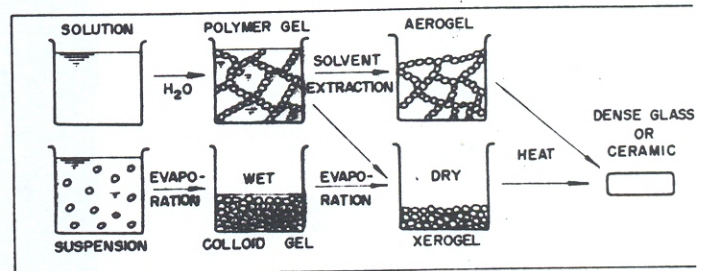
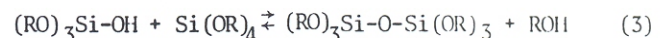
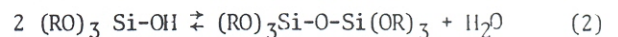
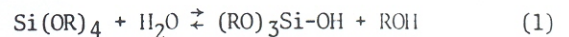


Figure 1. Schematic SG Process

Synthesis. Solution/sol-gel processing of glass and ceramics uses metal alkoxides of network forming cations ($M(OR)_x$ where M is Si, B, Ti, Al, etc., and R is often an alkyl group) as soluble, ceramic precursors. In alcohol/water solutions the alkoxide groups are removed stepwise by acid or base catalyzed hydrolysis reactions and replaced with hydroxyl groups (Eq. 1). Subsequent condensation reactions involving the hydroxyl groups yield macromolecular solution species composed of inorganic oxide linkages (Eqs. 2 and 3).



Gelation typically occurs by a secondary process in which these primary species link together to form a network extending throughout the solution. At the gel point, physical properties of the system such as viscosity and elastic moduli diverge.

Bulk gels (monoliths) are made by casting a solution in a mold followed by gelation and drying (Figure 1). If drying occurs by evaporation of the solvent, the network collapses somewhat and the resulting

product is termed a xerogel. If the solvent is removed under supercritical conditions, shrinkage is minimized and the resulting expanded gel is termed an aerogel.

Colloidal gels are formed from metallic salt solutions (chlorides, nitrates, etc.) and oxide or hydroxide sols. The commonly used techniques involve destabilization of colloidal sols.

Hydrolysis. For single alkoxides, the hydrolysis rate generally decreases with increasing length of the n-alkyl chain and with increasing branching of the alkyl group. Hydrolysis is catalyzed by both acids and bases, in each case reflecting a nucleophilic attack on the electrophilic silicon atom. Since alcohol is produced in the hydrolysis reaction, use of alcohol as a solvent can result in the hydrolysis remaining incomplete even in the presence of free water in the system.

Polymerization. The polymerization of metal hydroxides or hydroxides and alkoxides is a poorly understood process which depends strongly upon the metal atom, the temperature, solvent, concentration of hydroxide or alkoxide and water as well as the presence of catalysts.

For cations other than silicon, almost nothing is known in detail about the kinetics of polymerization, nor about the effects of acid or base catalysis on polymerization kinetics, nor about the structural features present at various stages of polymerization. Further information in this area would be of considerable benefit in future developments. In many instances, gelation is viewed simply as a coalescence of relatively dense colloidal particles; and the approach of viewing gelation as a polymerization process is neglected.

Drying. Following either the colloidal or solution gel route to fabrication of glass or ceramic bodies, one has to eliminate the solvent and undesirable atoms, including carbon and hydrogen in alkoxide syntheses and anion in salt syntheses. The former are eliminated by heat + oxygen and the latter by leaching.

When a gel is dried, stresses develop which very often lead to fracture of the body. These stresses result from non-uniform shrinkage and capillary forces. The effect of volume changes on stresses produced during drying has been proposed by Cooper [4] and substantially developed and improved by Scherrer in a series of articles summarized in [5]. He demonstrated that drying stresses are proportional to the evaporation rate and size of the body, and inversely proportional to the permeability and the bulk modulus. They also depend on the shape of the body. To avoid cracking the drying rate must be slow. Larger pore sizes and a stronger gel network tend to reduce the amount of cracking. Drying is the most difficult and time-consuming step in the preparation of bulk pieces from gels.

Firing and Sintering. Once a dried gel is obtained, for most applications, it must be heat treated to convert it to a dense body (unless a porous material is desirable for applications such as ultrainsulators or catalytic converters). In this case one benefits from the much lower temperatures required when compared with an equivalent precursor obtained by the traditional ceramic route.

During firing any of the following reactions may occur: decomposition of salts; carbonization or combustion of residual organic groups; desorption of absorbed solvent from the walls of micropores; dehydration (polymerization); formation of micropores or even foams from gas generation; collapse of micropores; and sintering and densification.

The firing of gel monoliths leads to a generalized densification of the structure. The principal process involved is densification of the structure. The main mechanism in densification is often viscous sintering; and models have been employed to describe such sintering. The first due to Mackenzie and Shuttleworth [6] is most applicable for the late stages of densifi-

cation when the pores are closed and isolated. The second, suggested for very open structures of high porosity, was originally developed by Scherrer [7] to describe the sintering of soots produced by flame hydrolysis. This model represents the structure as a cylindrical array, and employs the Frenkel [8] assumption that the rate of energy dissipation in viscous flow equals the rate of decrease in surface area.

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). The competition between viscous sintering and crystallization has been described by Uhlmann and co-workers [9, 10]; and crystallization during the heat treatment of gels has been evaluated by Zarzycki [11]. In the case of gels, the description of crystallization is complicated by the expected variations of the nucleation rate and crystal growth rate with time and water content.

APPLICATIONS

In spite of intensive research activities only a few commercial products are manufactured by the SG technology. These include ultrafine powders, bio-hydroxyapatites for dental and bone restorations, nuclear fuel pellets (e.g. ThO_2 and related oxides), glassy and crystalline fibers (B_2O_3 - Al_2O_3 - SiO_2), abrasives based on Al_2O_3 and anti-reflective oxide coatings on glasses.

The potential applications, however, include a large variety of composites, porous solids, fibers, thin and thick films as recently summarized by Mackenzie [12]. Several promising uses are related to thin oxide coatings for electronic and optical applications [3,12]. These include, a) Electronic Applications: dielectrics and piezoelectrics (BaTiO_3 , SrTiO_3 , PZT, doped titanates and zirconates, etc.), PTC materials (e.g. doped BaTiO_3), varistors (e.g. Bi_2O_3 - doped ZnO), ferrites, substrates (Al_2O_3 , mullite, cordierite), sensors (TiO_2 and BiO_2 based), solid electrolytes (novel glasses), b) Optical Applications: optical waveguide preforms, glasses with novel index-dispersions relations, electropical films (LiNbO_3 , BaTiO_3 , KTP), c) Other Applications: conductive, passivation, barrier, anti-reflection, oxidation and corrosion resistant coatings.

CONCLUSIONS

The sol-gel technology is a highly interdisciplinary field and is one of the most promising techniques for the production of advanced ceramics and glasses, specially composites, porous materials, fibers and thin films. Some commercial products already exist and an impressive number of (potential) successful applications still depend on scientific understanding and control of the various stages of the process, as well as on the availability of cheaper precursor chemicals. The use of colloidal gels might be a milestone in this last aspect. There is little doubt that tremendous progress will be achieved in the near future.

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