Sol-Gel Processing of Ceramic Films

Dennis Gallagher and Terry A. Ring*

Ceramic films are important for optical and protective coatings and are increasingly important for the production of electronic devices. For many applications, the film can be deposited from sol-gel solutions. This review discusses the stages of processing ceramic films, from the formation of the precursor solutions to the final thermal treatment to produce the ceramic. By controlling the solution chemistry and coating conditions, the microstructures formed can be tailored and thus the final properties of the films controlled. The sol-gel route requires relatively low processing temperatures and therefore can be applied to a wide variety of substrate materials.

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1. Introduction

In traditional ceramic processing, objects are produced using mineral powders that are mixed together with additives to form the final shape before heat treatment. At high temperatures, these minerals sinter or melt, and often undergo solid state reactions to form new phases not in the starting minerals. This traditional processing route is the subject of another review article[27] in this issue of Chimia. Our paper describes the processing of ceramic materials directly from sol-gel solutions with emphasis being placed on making ceramic films. The processing of ceramics directly from solutions, rather than minerals, has become a popular fabrication method for those materials which require purity and homogeneity not easily achieved by traditional routes.

Most work in chemical processing of materials has been on the production of powders[27]. Precipitating a powder from solution avoids one of the fundamental problems associated with sol-gel processing: the separation of the ceramic from large volumes of liquid which are trapped in the gel structure. Sol-gel solutions can also be applied directly to the formation of fibers, low density monolithic materials, and as surface treatments for powders or fibers. Another direct use of sol-gel solutions is in the deposition of ceramic films onto substrates. Here the traditional disadvantages of solution processing (e.g. the higher cost of raw materials) are alleviated by the low volumes of material used in the forming of layers. For these reasons, sol-gel coatings are used in making glass and ceramic coatings on substrates as an alternative to the chemical vapor deposition and sputtering processes.

The earliest routes for forming ceramics from sol-gel solutions involved the precipitation of metal oxide particles from solutions. These form a true colloidal suspension – a *sol*. Upon aggregation of sols, a network is formed, a *gel,* which is intermediate between a solid and a liquid state. The term *Sol-Gel* has since been used by the materials science community to describe, albeit erroneously, virtually all chemical processing of ceramics from solutions.

The schematic diagram in Fig. 1 and micrographs in Fig. 2 demonstrate the possible variations in sol-gel processing. There are a variety of chemical systems from which the starting solution may be made. These include metalorganic, polymeric, and ionic solutions. The chemistry chosen dictates the physical characteristics of the film produced. These characteristics include its structure, specifically, the density distribution in the gel network. The networks formed may be described as:

– *Polymer Networks* giving low and uniform density distributions formed by crosslinking polymers.
– *Aggregate Networks* giving low and non-uniform density distributions formed by clustering of aggregates.
– *Particle Networks* giving high and non-uniform density distributions formed by the flocculation or sedimentation of particles. The surface chemistry of the particles controls their suspension properties and their floc structure.

In this review, we will discuss the various stages of sol-gel processing with examples drawn from the formation of ceramic films.

2. Precursor Solution Chemistry

Ceramic materials are made from the oxides, nitrides, carbides, or sulfides of metals. The precursor solution must contain both the metal and the requisite O, N,

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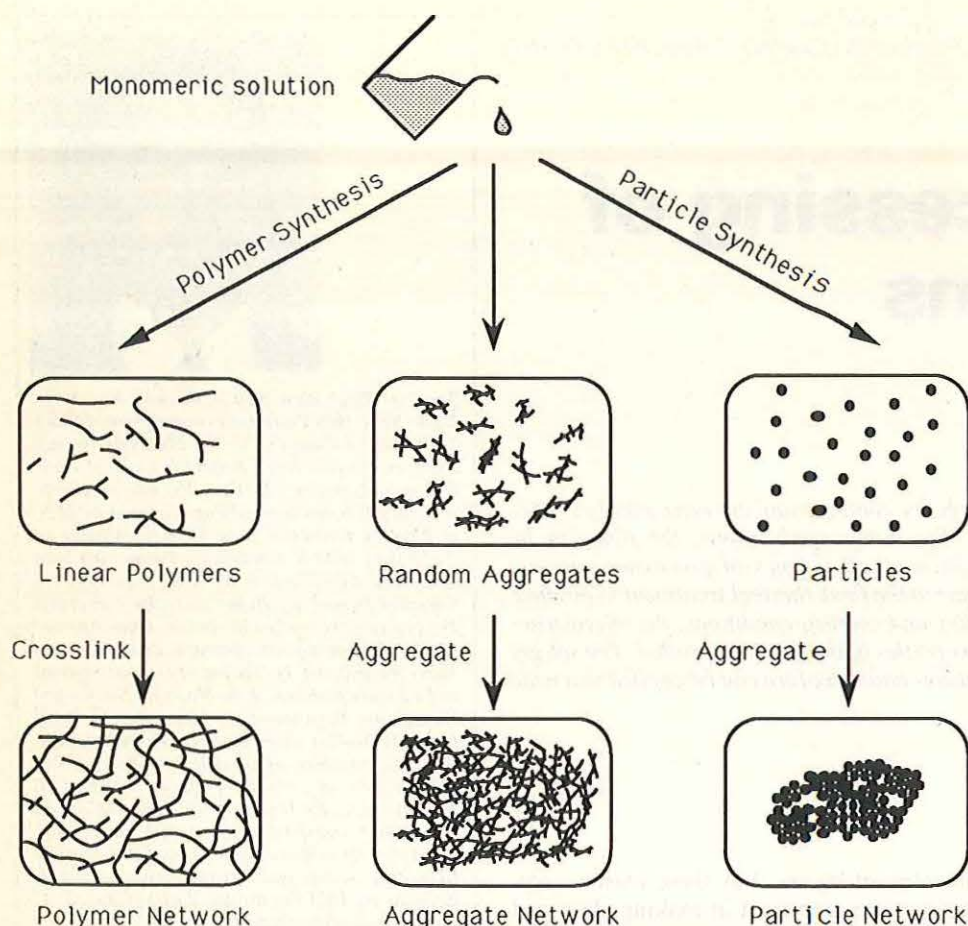École Polytechnique Fédérale de Lausanne
CH–1015 Lausanne

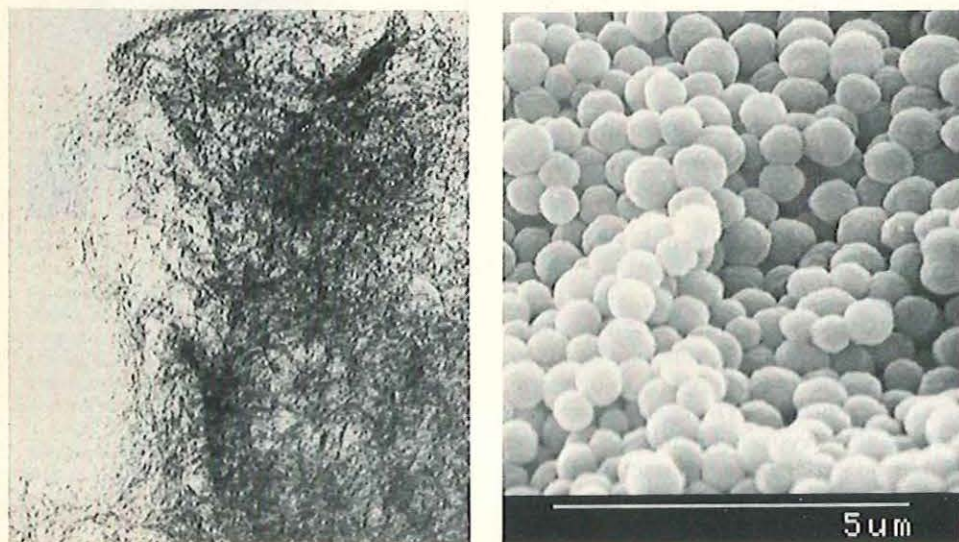Fig. 1. *Schematic diagram of routes for structural evolution of metallorganics in solution.*

Fig. 2. *Left: Transmission electron micrograph of aqueous alumina gel (125 000 ×)* [1]. – *Right: Scanning electron micrograph of sol-gel tinania spheres* [2].

C, or S in close liaison. Two broad classifications based on the physical properties of the precursor solution will be used: 1) true solutions where the metal ion does not form a network, and 2) solutions which polymerize to form a network. Both types of solutions can be used to form ceramic thin films.

2.1. True Solutions

The true solutions are those in which the metal ion is complexed to allow solubility. This complex does not react further to form a network. In these solutions the viscosity, which is important in film formation, is controlled by the concentration of the metal ion complex. When metal salts or

complexing molecules are incompatible with one another, undesirable precipitation and segregation may occur during drying.

Common complexing agents are bidentate ligands such as citric or oxalic acid, or a quaterdentate ligand such as ethylenediaminetetraacetic acid (EDTA). An example of complexation is the formation of a yttrium, barium, and copper solution which is a precursor to the $YBa_2Cu_3O_{7-x}$ superconducting phase. The highest concentration possible for the metal nitrates of Y, Ba, and Cu combined in solution is less than 10^{-1} M in Cu. With EDTA as a complex for the poorly soluble Ba [3]

$$EDTA^{4\ominus} + Ba(NO_3)_2 \rightarrow \\ [Ba(EDTA)]^{2\ominus} + 2NO_3^{\ominus} \quad (1)$$
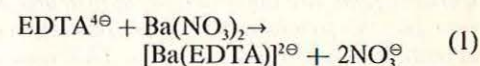
a $YBa_2Cu_3O_{7-x}$ solution with a solubility of 1M in Cu at pH 9.5 can be formed.

Some metallorganic salts, like 2-ethylhexanoates, naphthenates, and acetylacetonates, are also soluble at high concentrations in organic solvents. For example Ba and Cu ethylhexanoates, $[M\{OOCCH(C_2H_5)C_4H_9\}_2]$ and Y naphthenate $[Y(OOCC_{10}H_7)_3]$ are completely soluble in trichloromethane and are used as a precursor to the $YBa_2Cu_3O_{7-x}$ superconducting phase [3].

2.2. Network Forming Solutions

Solutes which form networks in solution give rise to a gel. The precursors most often used in the sol-gel process are hydrolyzed alkoxides in alcohol solutions. A short discussion of the alkoxide chemistry is useful to explain their gelling characteristics.

The alkoxide precursors are commonly formed as one of a series of homoleptic alkoxides $M(OR)_n$ where n = 1–6. Organic molecules such as alcohols tend to be strong p-donors and thus stabilize the highest oxidation state of the metal [4]. The specific synthesis route of an alkoxide is dictated by the electronegativity of the metal. The most common routes for metal alkoxide formation are [5]:
- Reduction of alcohols for electropositive metals.
- Substitution on metal halides for electronegative metals.
- Catalyzed reaction with labile M–NR_2 or M–C bonds [4] for less active metals.

The electronegative metals usually form unstable alkoxides which tend to polymerize rapidly to form $[-M(OR)_2-O-]_n$. Solid alkoxides are easily solubilized in alcohols. Alkoxide precursors must be kept dry to avoid hydrolysis, which is the first step in the reaction of alkoxides to form networks. This is difficult because alkoxide solutions easily absorb water from the atmosphere.

An example of an alkoxide solution prepared as a $YBa_2Cu_3O_{7-x}$ precursor solution is given by *Zheng* et al. [6]. They used Y, Ba, and Cu isopropyloxy compounds in

Heterometallic complexes which contain an M'–O–M'' linkage can also be formed in solution, allowing multi-metal ion gel networks to be formed; for example a Pb-Ti alkoxide has been prepared by the reaction of tetraisopropyl titanate [Ti(OC$_3$H$_7$)$_4$] with lead acetate [Pb(C$_2$H$_3$O$_2$)$_2$·3H$_2$O] in methoxyethanol[14]. This alkoxide complex is used in forming PbTiO$_3$. Solutions may also be partially prehydrolyzed and mixed to control the reaction kinetics and avoid segregation. Prehydrolysis can help circumvent the problems of different reaction rates in multi-alkoxide systems.

Gelation is initiated by chemical reactions among precursor molecules, changes in solution chemistry, or evaporation of solvent. But irrespective of the process by which it is attained, the gelation of a precursor solution begins with the formation of fractal aggregates of the discrete units present in solution (monomers, oligomers, polymers, or particles). *Brinker* and *Scherer*[15] have described the gelation process as one in which these aggregates grow to the point at which they impinge on one another and link, forming a network. Though reactions may not be completed, the point at which a single aggregate cluster appears to encompass the entire solution is defined as the gel point.

A model for gelation comes from the mathematics of percolation theory, where molecular groups are represented as points on a lattice and bonds are formed randomly with probability P between nearest neighbor lattice sites[16]. This eventually leads to the forming of a random cluster which spans the lattice. The percolation threshold is analogous to the gel point seen in polymeric systems. At gelation, the chemical reactions may not be complete. The continuation of reactions is referred to as ageing and usually reinforces the network. The sol-gel transition in alkoxides is not reversible. After the formation of the network, many characteristics of the structure are set, but some may still be altered during deposition, drying, and thermal decomposition.

4. Film Formation

After forming the solution, the next step in sol-gel processing is film formation. There are many aspects to the processing of films which are common to all the deposition techniques. *Schroeder*[17] has outlined the conditions necessary for thin film formation: The solution must wet the substrate, it must remain stable with ageing, it should have some tendency towards crystallization into a stable high-temperature phase, and for multiple layers the previous layers must be either insoluble or heat treated to make them insoluble before subsequent depositions.

For a solution to wet a substrate the contact angle θ between the surface of a drop of solution and the substrate must be less than 90°. The conditions for this to occur are described by *Young*'s equation:

$$\gamma_{LV}\cos\theta = \gamma_{SV} - \gamma_{SL} \qquad (6)$$

where γ is the surface tension for the liquid-vapor, solid-vapor, and solid-liquid interfaces respectively. For wetting, the easiest variable to control is the surface tension of the solution. Alcohol solutions used with metal alkoxides wet better than aqueous solutions because they have lower surface tensions.

The method of depositing a solution onto a substrate also affects the microstructure of the film. Flow due to gravitational and centrifugal draining of the solvent before drying can cause shear which deforms the network. The capillary forces at the meniscus between substrate and solution in dip coating also acts to shear the network. The effect of shear is to restructure clusters and induce interpenetration or alignment of polymer[18]. Whether the network formation occurs in the early stages of deposition rather than later dictates how much of an effect the deposition technique has on structure.

The effect of structure on the character of the final film is summarized in Fig. 5. A solution of linear and randomly branched polymers, as shown in Fig. 5A, forms a highly stable and concentrated solution which gives a high and uniform density film. The linear polymers align themselves with the applied shear stress from spin or dip coating, and pack into an even higher density structure. The fine pore structure created in gelation increases the capillary forces during solvent removal which increases the density and reduces pore volumes. These are important characteristics for protective and electronic coatings.

Fig. 5B shows the character of a film formed from aggregates in solution. Aggregates have a low and non-uniform density distribution. To prevent gelation they must be used at a high dilution. The higher dilution decreases the amount of material being deposited at the substrate surface. During solvent evaporation aggregation occurs. This leads to larger pores, higher pore volumes, and lower densities. These are desirable film characteristics for catalysts, anti-reflective coatings, and sensor materials such as surface acoustic wave devices which respond to the absorptive nature of the film.

In gelled sols as shown in Fig. 5C, the voids of the film are very large since the packing of the gelled aggregates is only improved slightly by the shear forces during deposition. These films sinter well with low stresses giving high density films. These are useful properties for making thick and protective films.

Polymerizable systems, like the metal alkoxides, are interesting because it is possible to form all of these different film structures by simply manipulating the solution chemistry. Properties such as structure, viscosity, and concentration are easily controlled with polymers and there are fewer problems with the precipitation or segregation of phases. One of the most important coating variables is the solution rheology. It effects the films thickness and evenness during deposition.
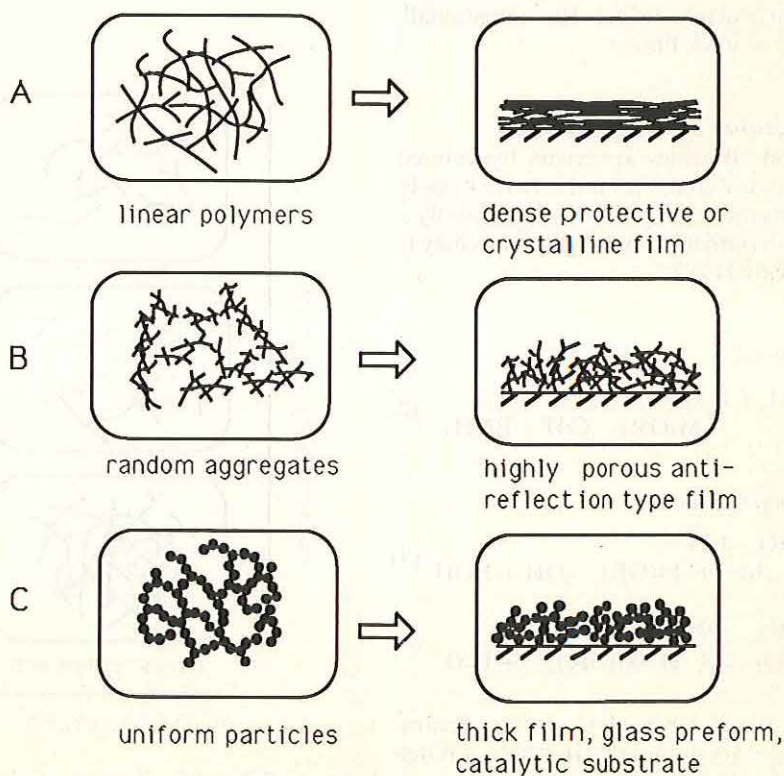

A linear polymers → dense protective or crystalline film

B random aggregates → highly porous anti-reflection type film

C uniform particles → thick film, glass preform, catalytic substrate

Fig. 5. Schematic diagram showing the relationship between gel structure and film structure.

propanol which was further modified by the addition of an organic acid chelating agent. The chelating agent stabilizes the alkoxides with respect to hydrolysis.

Polymer network solutions can also be formed from aqueous chemical systems. Aqueous metal chelates that have at least one additional carboxy group as a reaction site, can undergo polyesterification with a polyhydroxy alcohol to form a network [7,8]. Aqueous metal ions can also react with poly(acrylic acid) and be precipitated as a crosslinked polymer [9]. The polymerization mechanism, and its rate, are important factors in determining the molecular weight of the polymers and the density distribution of the microstructure formed.

3. Microstructure Development

The next stage in processing ceramic films from solution is the development of structure. There are two types of structure development to consider: 1) the structure of the primary aggregate or polymer, and 2) the structure which develops upon gelation. It is possible to control both types of structure development through the chemistry of the precursor solutions. The control of structure is essential to achieve the solution rheology necessary for film formation and to determine the final microstructure of the dried film.
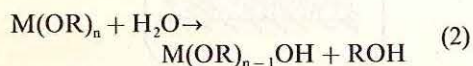
3.1. True Solutions

A true solution used for ceramic coatings will precipitate and aggregate during solvent evaporation. This aggregated precipitate is deposited onto the surface of the substrate forming a film. Precursor solutions which form structures in this manner are particularly useful for intentionally porous or thick films.
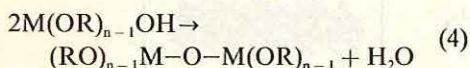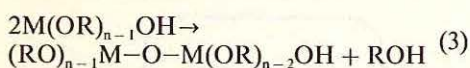
3.2. Network Forming Solutions

Metal alkoxides are easily hydrolyzed. Once hydrolyzed, they polymerize by poly-condensation mechanisms. The hydrolysis and polycondensation mechanisms may be represented as [10]:

Hydrolysis

$$M(OR)_n + H_2O \rightarrow$$
$$M(OR)_{n-1}OH + ROH \quad (2)$$

Polycondensation

$$2M(OR)_{n-1}OH \rightarrow$$
$$(RO)_{n-1}M-O-M(OR)_{n-2}OH + ROH \quad (3)$$

$$2M(OR)_{n-1}OH \rightarrow$$
$$(RO)_{n-1}M-O-M(OR)_{n-1} + H_2O \quad (4)$$

where the R is an alkyl group. Because alkoxides are immiscible in water, it is necessary to put the alkoxides and water into a mutual solvent such as an alcohol for the

hydrolysis reactions to occur.

The relative rates of reaction for the hydrolysis and condensation dictate the structure and properties of an alkoxide gel. These reaction rates are schematically described in Fig. 3 for the example of a silicon ethoxide. In acidic solutions hydrolysis is achieved by a bimolecular displacement mechanism which substitutes a $H^{\oplus}$ (hydronium ion) for an alkyl group (R) [12]. Under these conditions the hydrolysis is rapid compared to the condensation of the hydrolyzed monomers and promotes the development of larger and more linear molecules, as is described in Fig. 4. Under basic conditions hydrolysis occurs by nucleophilic substitution of $OH^{\ominus}$ for alkyl

groups [13]. Here the condensation is rapid relative to hydrolysis, promoting the precipitation of three-dimensional colloidal particles as shown in Fig. 2b (titania spheres).

In addition to adjusting pH, the reaction rates may be varied by the temperature, water concentration, and the choice of alkoxide ligands. The steric interactions of the alcohol solvent chosen also influences the rates. If the alcohol solvent is different from that of the alkoxide ligand, transesterification may modify the reaction rates. For example [4]:

$$M(OEt)_n + mPrOH \rightarrow$$
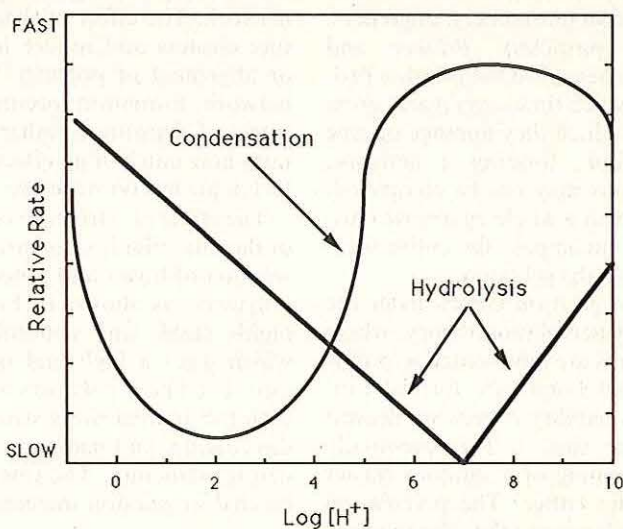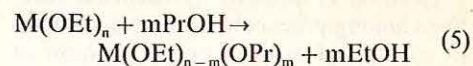$$M(OEt)_{n-m}(OPr)_m + mEtOH \quad (5)$$

Fig. 3. Schematic comparison between the rates of hydrolysis and condensation for silicon ethoxide solutions (from Schaefer [11], Copyright 1989 by the AAAS).
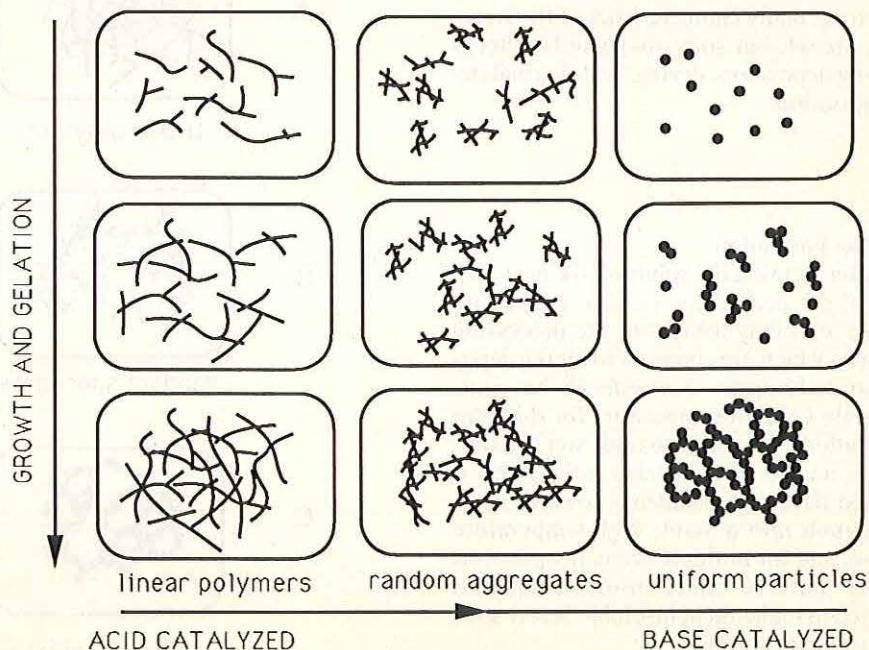

Fig. 4. Schematic diagram of the effect of pH on the growth and gelation of a silicon ethoxide.

be added to the solutions which reduce drying stress. These are known as drying control chemical additives (DCCA)[22]. In general, these additives either reduce capillary pressure at the gel surface, reduce the solvent vapor pressure, or modify the pore size distribution. Another technique is to use hypercritical evacuation[23]. Above the critical temperature and pressure of the solvent, there is no longer a liquid/vapor interface and therefore no capillary pressure to cause shrinkage. Gels formed under these conditions are called aerogels. With the film constrained by a substrate, all shrinkage during drying is normal to the surface of the substrate. If thin enough (< 0.5 μm), films tend not to crack upon drying. *Lange*[24] hypothesizes that since crack growth is a function of the stress relieved per unit volume, a low volume of material, as in films, makes crack growth an unfavorable process[15].

6.2. Thermal Decomposition

As the gel increases in temperature, weight is lost from the degradation of the sol-gel network. An example of weight loss from a sol-gel system is given in Fig. 8. At low temperatures, up to about 150°C, there is the loss of the solvent, physically adsorbed water, and weakly bound ligand molecules. The fine porosity of the matrix slows down the liberation of these molecules past the temperature when they normally volatilize.

Above 250°C pyrolysis of the molecular network begins. The volatilization of the decomposition products of ligand groups is responsible for the weight loss. The structure decomposes first by cleavage of the weakest bonds[25]. The decomposition temperature varies with bond strength, crosslinking, and structure of the groups effected, as well as the atmosphere in which it takes place. Different chemical structures have different decomposition behaviors. Fig. 8 shows the thermal decomposition of a Ba- and Cu-ethylhexanoates and Y-naphthenate solution in trichloromethane. Each of the metal carboxylates has a different decomposition profile when measured separately. When the weight loss of each component is added up in the appropriate proportions for the composite solution, the profile is different than that observed experimentally for the solution. Interactions between the different metal carboxylates in solution cause slight changes in decomposition temperatures of the components and there is also an overlap of the separate decomposition temperatures. The pyrolysis stage results in an amorphous and homogeneous solid.

In the absence of oxygen, or presence of difficult to decompose molecular structures, residual organic groups form chars which remain in the structure until high temperatures. Above 800°C, this residual organic is removed by decarbonation. Carbon is difficult to remove completely and the presence of carbon and other chemical residues in the final piece is normal.

6.3. Sintering

With decomposition, the collapse of the skeleton begins and this eventually leads to the complete consolidation by sintering. Since gels are amorphous the dominant sintering mechanism is viscous flow. Viscous flow is a much faster mechanism than the diffusion in crystals and this contributes to lower sintering temperatures in gels as compared to sintering of mineral powders. *Scherer*[26] has studied viscous sintering of porous gel networks and concluded that the rate of contraction for the network $\dot{\varepsilon}$ varies with:

$$\dot{\varepsilon} \propto \frac{\gamma_{sv} N^{1/3}}{\eta} \qquad (9)$$

where γ_{sv} is surface energy of the gel, η is the viscosity, and N is the number of pores per unit volume. As one decreases the pore size, keeping the density constant, the number per unit volume increases and as a result the gel sinters faster. Another observation is that viscosity decreases with increasing temperature, and increases with the degree of crosslinking. But if one heats the sample fast, the effects of crosslinking are minimized and sintering is enhanced. Though rapid heating may be detrimental in bulk materials because of trapped pores, this is not a problem of the same magnitude in thin films. It is also important to sinter to full density before crystallization occurs which reduces the sintering rate.

7. Conclusion and Outlook

This overview of the processing technology for sol-gel films has focused on the effects of solution chemistry and network structure in forming a sol-gel film. The structure formed, its deposition, and its thermal treatment all offer opportunities to affect the final properties. This flexibility is one of the unique advantages to the application of sol-gel processing to forming films.

It can be expected that this technology will find uses beyond the current applications such as anti-reflective films in window glass, to areas such as corrosion resistance coatings and electronic devices in the near future. With these new applications, more complex multi-oxide films and difficult to control chemistries will need to be investigated. Compositions such as indium tin oxide for transparent conductive layers, TaO_2 for protective coatings in corrosive chloroalkali processing, TiO_2 as photochemical catalysts, and SiO_2 in surface acoustic wave devices present challenging problems in controlling chemistries and structures. In order to successfully develop the technology required for these new applications, a better understanding of the physical chemistry of the precursor solutions and the film formation will have to be obtained.
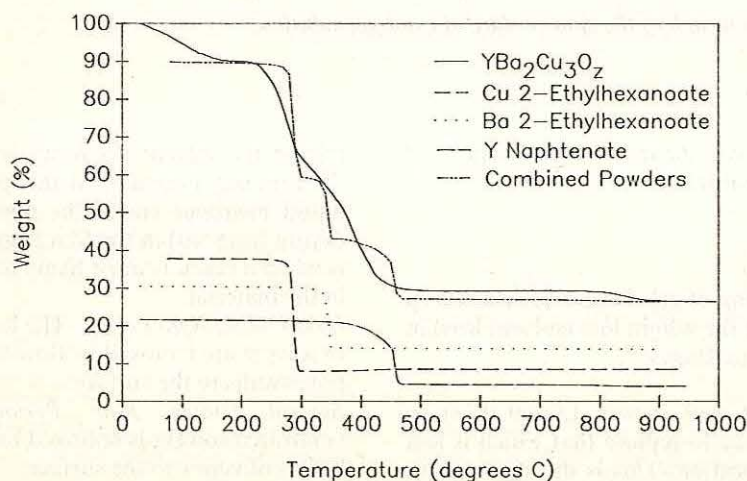
[1] Versal™ alumina gel, photo by courtesy of Kaiser Aluminium and Chemical Company.
[2] R. Benfer, «Continuous Flow Reactor for Titania Powder», M.S. thesis, Massachusetts Institute of Technology, Cambridge MA (1986).
[3] C. Barbe, T.A. Ring, unpublished results.
[4] P. Colomban, «Gel Technology in Ceramics, Glass-Ceramics, and Ceramic-Ceramic Composites», *Ceramics Int.* 15 (1989) 23.
[5] H. Okamura, H.K. Bowen, «Preparation of Alkoxides for the Synthesis of Ceramics», *Ceramics Int.* 12 (1986) 161.
[6] H. Zheng, M.A. Colby, J.D. Mackenzie, «The Control of Precipitation in Sol-Gel Solutions», in: *Better Ceramics Through Chemistry III* (Eds. C.J. Brinker, D.E. Clark, D.R. Ulrich), Mater. Res. Soc. Symp. Proc. Vol. 121 (1988) 537.
[7] M.P. Pechini, «Method of Preparing Lead and Alkaline Earth Titanates and Niobates and Coating Method Using the Same to Form a Capacitor», U.S. Patent 3330697 (July 11, 1967).

Fig. 8. Thermogravimetric analysis of superconducting $YBa_2Cu_3O_{7-x}$ film solution and the raw materials used to form the precursor solution: yttrium naphthenate, barium 2-ethylhexanoate, and copper 2-ethylhexanoate[3]. *The raw materials curve is a calculated from proportions of raw materials in the composite film solution.*

5. Coating Techniques

Although there are many factors controlled by the network structure in solution, the deposition parameters are also important to the final properties of a film. Therefore, we will discuss the critical variables in the most common techniques for deposition from solution: dip and spin coating.

5.1. Dip Coating

Dip coating is the term applied to describe all techniques where a substrate is withdrawn from a solution. Fig. 6 demonstrates the coating of a substrate and schematically shows the factors which effect film thickness. Scriven [19] has reviewed these factors and gives the following equation to govern the thickness (h) of the deposited layer:

$$h = 0.944 \left(\frac{\eta\mu}{\sigma}\right)^{1/6} \left(\frac{\eta\mu}{\rho g}\right) \qquad (7)$$

where ρ is the density of the solution, η viscosity, g gravitational constant, μ is the withdrawal speed, and σ is surface tension. This equation does not include terms for solids concentration, effects of evaporation, or angle of inclination. But it does indicate that thickness will increase with withdrawal speed as is observed experimentally by Strawbridge and James [20]. If the withdrawal speed is too low, viscous drag can keep the solution from wetting the substrate.

5.2. Spin Coating

In the spin coating method, solution is dripped onto a spinning substrate and is then spread by centrifugal force evenly across the surface as seen in Fig. 7. This technique is less economical than dipping because excess solution is lost during deposition and it is not a continuous process. Spin coating is more suitable for coating small disks and lenses. Many of the same factors in the dipping of films apply here as well. Meyerhofer [21] has studied the factors effecting film thickness and predicts:

$$h \propto f^{2/3} \eta_i^{1/3} e^{1/3} \qquad (8)$$

where f is the spin rate, η_i is the initial viscosity, and e is the evaporation rate. Because the evaporation rate itself varies with spin rate ($e \propto f^{-1/2}$), attempts to predict thickness are complicated.

6. Thermal Treatment

The final stages for processing a ceramic film from a sol-gel solution are drying and heating of the deposited material to form the ceramic phase. Many complex interactions with the substrate and the atmosphere, as well as transformations within a film take place at this stage. Since these effects are system specific, the discussion
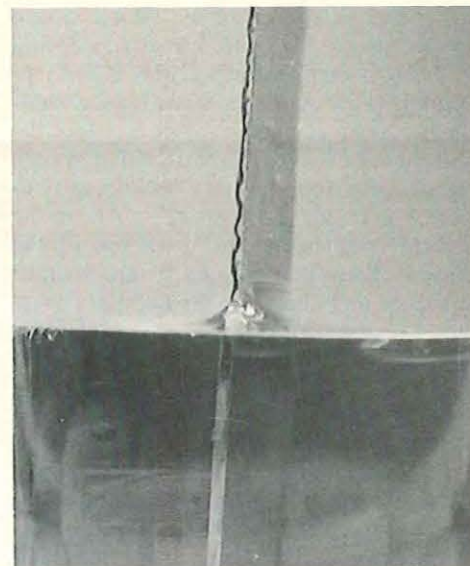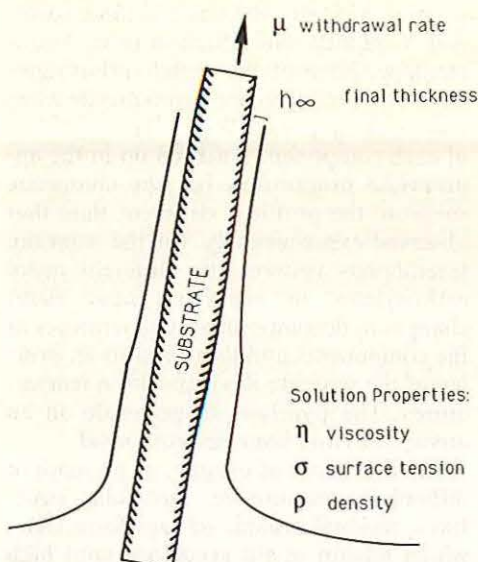

Fig. 6. Left: Schematic diagram of substrate and interactions with solution during dipping. – Right: Photograph of sol-gel solution during dip coating.
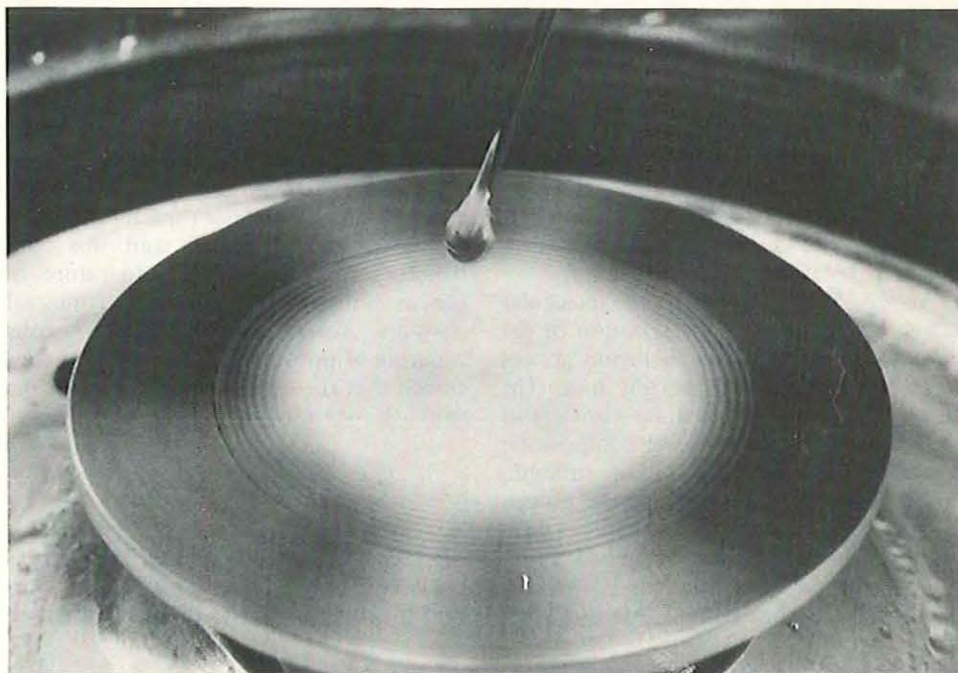
Solution Properties:
η viscosity
σ surface tension
ρ density

μ withdrawal rate
h_∞ final thickness

Fig. 7. Photograph of the spin coating of a sol-gel solution.

will only cover the more general aspects of thermal treatment.

6.1. Drying

The drying of gels is best described as a function of the weight loss (solvent loss) in the following stages [15]:

– Constant Rate Period: Liquid flows to the surface to replace that which is lost to evaporation. This is the stage where most shrinkage and warping occurs as a result of the capillary pressure differentials within the film.
– Critical Point: The gel matrix reaches a point where it can no longer shrink to release the solvent necessary to reduce the capillary pressure. At this point the liquid meniscus enters the matrix and drying from within the film begins. This is when a crack is most likely to appear in the material.
– First Falling Rate Period: The last layers of solvent are removed by flow along the pores walls to the surface.
– Second Falling Rate Period: The volatilized solvent is removed by the diffusion of vapor to the surface.

The timing of these stages is intimately linked to the structure of the film.

There are several ways to reduce cracking during drying of gels. Chemicals may

[8] P.A. Lessing, «Mixed-Cation Oxide Powders via Polymeric Precursors», *Am. Ceram. Soc. Bull. 68* (1989) 1002.

[9] A.L. Micheli, «Synthesis of Ceramic Powders Using an Aqueous Organic Polymer Precursor», *Ceramics Int. 15* (1989) 131.

[10] J. Livage, M. Henry, «A Predictive Model for Inorganic Polymerization Reactions», in: *Ultrastructure Processing of Advanced Ceramics* (Eds. J.D. Mackenzie, D.R. Ulrich), Wiley, New York (1988), p. 183.

[11] D.W. Schaefer, «Polymers, Fractals, and Ceramic Materials», *Science 243* (1989) 1023.

[12] E.R. Pohl, F.D. Osterholtz, «Kinetics and Mechanism of Aqueous Hydrolysis and Condensation of Alkyltrialkoxysilanes», in: *Molecular Characterization of Composite Interfaces* (Eds. H. Ishida, G. Kumar), Plenum Press, New York (1985), p. 157.

[13] E.J.A. Pope, J.D. Mackenzie, «Sol-Gel Processing of Silica II. The Role of the Catalyst», *J. Non-Cryst. Solids 87* (1986) 185.

[14] J.B. Blum, S.R. Gurkovich, «Sol-Gel-Derived PbTiO₃», *J. Mater. Sci. 20* (1985) 4479.

[15] C.J. Brinker, G.W. Scherer: *Sol-Gel Science*, Academic Press, New York, in press.

[16] D. Stauffer, A. Coniglio, M. Adams, «Gelation and Critical Phenomena», in K. Dusek (Ed.): *Advances in Polymer Science, Polymer Networks*, Vol. *44*, Springer, Berlin (1982), p. 103.

[17] H. Schroeder, «Oxide Layers Deposited from Organic Solutions», in: *Physics of Thin Films*, Vol. *5*, Academic Press, New York (1969), p. 87.

[18] C.J. Brinker, «Sol-Gel-Derived Thin Films», *Ceram. Eng. Sci. Proc. 9* (1988) 1103.

[19] L.E. Scriven, «Physics and Applications of Dip Coating and Spin Coating», in: *Better Ceramics Through Chemistry III* (Eds. C.J. Brinker, D.E. Clark, D.R. Ulrich), Mater. Res. Soc. Symp. Proc. Vol. 121 (1988) 717.

[20] I. Strawbridge, P.F. James, «Glasses from Alkoxide Derived Gels», in *Novel Ceramic Fabrication Processes and Applications* (Ed. R.W. Davidge), Br. Ceramic Proc. *38* (1986) 251.

[21] D. Meyerhofer, «Characteristics of Resist Films Produced by Spinning», *J. Appl. Phys. 49* (1978) 3993.

[22] L.L. Hench, «Use of Drying Control Chemical Additives (DCCAs) in Controlling Sol-Gel Processing», in: *Science of Ceramic Chemical Processing* (Eds. L.L. Hench, D.R. Ulrich), Wiley, New York (1986), p. 52.

[23] S.S. Kistler, «Coherent Expanded Aerogels», *J. Phys. Chem. 36* (1932) 52.

[24] F.F. Lange, «Criteria for Crack Extension and Arrest in Residual, Localized Stress Fields Associated with Second Phase Particles», in: *Fracture Mechanics of Ceramics, Vol. 2* (Eds. R.C. Bradt, D.P.H. Hasselman, F.F. Lange), Plenum, New York (1974), p. 599.

[25] G.T. Burns, T.P. Angelotti, L.F. Hanneman, G. Chandra, J.A. Moore, «Alkyl- and Arylsilsesquiazanes: Effect of the R group on Polymer Degradation and Ceramic Char Composition», *J. Mater. Sci. 22* (1987) 2609.

[26] G.W. Scherer, «Viscous Sintering of a Bimodal Pore-Size Distribution», *J. Am. Ceram. Soc. 67* (1984) 709.

[27] L.J. Gauckler, *Chimia 43* (1989) 290; H. Hofmann, *ibid. 43* (1989) 304; W. Rieger, *ibid. 43* (1989) 309.

[8] P.A. Lessing, «Mixed-Cation Oxide Powders via Polymeric Precursors», *Am. Ceram. Soc. Bull. 68* (1989) 1002.

[9] A.L. Micheli, «Synthesis of Ceramic Powders Using an Aqueous Organic Polymer Precursor», *Ceramics Int. 15* (1989) 131.

[10] J. Livage, M. Henry, «A Predictive Model for Inorganic Polymerization Reactions», in: *Ultrastructure Processing of Advanced Ceramics* (Eds. J.D. Mackenzie, D.R. Ulrich), Wiley, New York (1988), p. 183.

[11] D.W. Schaefer, «Polymers, Fractals, and Ceramic Materials», *Science 243* (1989) 1023.

[12] E.R. Pohl, F.D. Osterholtz, «Kinetics and Mechanism of Aqueous Hydrolysis and Condensation of Alkyltrialkoxysilanes», in: *Molecular Characterization of Composite Interfaces* (Eds. H. Ishida, G. Kumar), Plenum Press, New York (1985), p. 157.

[13] E.J.A. Pope, J.D. Mackenzie, «Sol-Gel Processing of Silica II. The Role of the Catalyst», *J. Non-Cryst. Solids 87* (1986) 185.

[14] J.B. Blum, S.R. Gurkovich, «Sol-Gel-Derived PbTiO₃», *J. Mater. Sci. 20* (1985) 4479.

[15] C.J. Brinker, G.W. Scherer: *Sol-Gel Science*, Academic Press, New York, in press.

[16] D. Stauffer, A. Coniglio, M. Adams, «Gelation and Critical Phenomena», in K. Dusek (Ed.): *Advances in Polymer Science, Polymer Networks*, Vol. *44*, Springer, Berlin (1982), p. 103.

[17] H. Schroeder, «Oxide Layers Deposited from Organic Solutions», in: *Physics of Thin Films*, Vol. *5*, Academic Press, New York (1969), p. 87.

[18] C.J. Brinker, «Sol-Gel-Derived Thin Films», *Ceram. Eng. Sci. Proc. 9* (1988) 1103.

[19] L.E. Scriven, «Physics and Applications of Dip Coating and Spin Coating», in: *Better Ceramics Through Chemistry III* (Eds. C.J. Brinker, D.E. Clark, D.R. Ulrich), Mater. Res. Soc. Symp. Proc. Vol. 121 (1988) 717.

[20] I. Strawbridge, P.F. James, «Glasses from Alkoxide Derived Gels», in *Novel Ceramic Fabrication Processes and Applications* (Ed. R.W. Davidge), Br. Ceramic Proc. *38* (1986) 251.

[21] D. Meyerhofer, «Characteristics of Resist Films Produced by Spinning», *J. Appl. Phys. 49* (1978) 3993.

[22] L.L. Hench, «Use of Drying Control Chemical Additives (DCCAs) in Controlling Sol-Gel Processing», in: *Science of Ceramic Chemical Processing* (Eds. L.L. Hench, D.R. Ulrich), Wiley, New York (1986), p. 52.

[23] S.S. Kistler, «Coherent Expanded Aerogels», *J. Phys. Chem. 36* (1932) 52.

[24] F.F. Lange, «Criteria for Crack Extension and Arrest in Residual, Localized Stress Fields Associated with Second Phase Particles», in: *Fracture Mechanics of Ceramics, Vol. 2* (Eds. R.C. Bradt, D.P.H. Hasselman, F.F. Lange), Plenum, New York (1974), p. 599.

[25] G.T. Burns, T.P. Angelotti, L.F. Hanneman, G. Chandra, J.A. Moore, «Alkyl- and Arylsilsesquiazanes: Effect of the R group on Polymer Degradation and Ceramic Char Composition», *J. Mater. Sci. 22* (1987) 2609.

[26] G.W. Scherer, «Viscous Sintering of a Bimodal Pore-Size Distribution», *J. Am. Ceram. Soc. 67* (1984) 709.

[27] L.J. Gauckler, *Chimia 43* (1989) 290; H. Hofmann, *ibid. 43* (1989) 304; W. Rieger, *ibid. 43* (1989) 309.