Sol–Gel Synthesis and Processing

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Sol-Gel Synthesis and Processing

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COVER PHOTO: *"Morphology of alumina foams treated at 1300°C," is courtesy of G.S. Grader, Y. de Hazan, and G.E. Shter, and appears as figure 6 in their paper, "Ultra Light Ceramic Foams," which begins on page 161.*

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Preface

This book is dedicated to Professor Rustum Roy of The Pennsylvania State University, who has been using the sol-gel process for making ceramics via mixing in solution, gelation, desiccation, and firing since 1948. Dr. Roy's review of the sol-gel process published in the *Journal of the American Ceramic Society* in 1956 became a citation classic.

Today, in many conferences on ceramics, a significant number of papers utilize the sol-gel process. This symposium was held as a special golden anniversary of Roy's use of sol-gel process at the centennial meeting of The American Ceramic Society. A special feature of the symposium was the opening historical session followed by the recent advances in sol-gel synthesis and processing. The symposium has covered topics on historical aspects of sol-gel; electroceramic films by sol-gel process; basic and applied sol-gel science; porous materials through sol-gel processing; and sol-gel processing of ceramics, glasses and composites. This symposium has brought together scientists from different disciplines such as ceramic science, materials science, chemistry, and chemical engineering, and it covered the synthesis and processing of many kinds of materials. A total of 45 papers has been presented from a large number of universities, government laboratories, and private industry in 12 countries. The 23 papers published in the proceedings have been reviewed and divided into four sections. The first section deals with historical aspects of sol-gel, the second section deals with the electroceramic films by sol-gel process, the third section deals with porous materials through sol-gel processing, and the fourth and final section deals with the basic and applied sol-gel science and processing of ceramics and composites.

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Historical Aspects of Sol-Gel Processing

THE SOL-GEL PROCESS IN CERAMIC SCIENCE: EARLY HISTORY OF DISCOVERY AND SUBSEQUENT DEVELOPMENT

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ABSTRACT

This paper records the earliest history of the development of the sol-gel process as a means of making pure and extremely fine grained glass and ceramic materials starting from gels, originating from solutions (inorganic and organic). Such "solution sol-gel" science had as its original goal the achievement of precursor materials with maximum purity, compositional *homogeneity* and *reactivity* for research in ceramics. In technology, the major potential (which is not very large) has probably already been realized as far as bulk products are concerned.

Since 1982, the author has created a new goal for the sol-gel process: that of achieving materials of maximum *heterogeneity* in precursors; to which the term 'nanocomposities' was first applied by him. The latter part of this paper summarizes some of the fundamental reasoning for the use of monophasic and multiphasic gels and illustrates the emergence of new potential applications with several examples from real technology and recent work in the author's laboratory.

INTRODUCTION

This paper is not a review of the field. I was invited to present my personal involvement in the earliest history of the field and my perspective on it today. Every review on history presents in any case the perspective of the writer. I have written, earlier, such a review in Science(1). There are many well known books, e.g. by Iler(2) which combine historical elements, and others which have much scientific background e.g. Scherrer and Brinker.(3) Each has its own goals and perspective. A recent review by Wood and Dislich(4) reviews SSG-technology. It is a fine review by very experienced, distinguished writers prepared for patent

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purposes. The review goes back to ancient technologies vaguely manifest in archeological artifacts from 2000-4000 B.C. That review, because of the authors' perspective, omits the entire field of food, where humans for millennia daily encountered sols and gels from tofu and yogurt to milk itself. The scope of this present history is narrower. It is concerned with the making of ultrafine, reactive, very pure ceramic precursors of any composition, for research in ceramic science. That was my goal in 1947-48, when I became involved in this area. Our goals from the earliest years covered making such pre-cursors not only for the simplest unary systems: Al_2O_3 and SiO_2, but for forsterite, cordierite, feldspars, micas, clays with four and five components.

HISTORY OF SOLUTION-SOL-GEL SCIENCE

In the early nineteen-fifties in a comment at the presentation of a paper of mine my colleague Professor W.D. Kingery of M.I.T. jokingly remarked that I was attempting to create a new field of "solution ceramics." This was an accurate categorization of the topic I will discuss herein and the fact that it was regarded as far offbeat is definitively shown in the neglect of the topic by the materials research community *for two decades*. Materials research has advanced greatly by the creation of new materials and processes (and new instruments). The solution-sol-gel (SSG) process is probably the most widely used new process innovation in general ceramic science research, although its application in industry is minuscule compared to, say, glass ceramics. SSG-derived ceramics are a subset of novel materials made by atomic scale mixing in solution of the constituents. The history of the topic therefore has three parts: first the concept of mixing in solution, and second the utilization of the gelation as a step in the process to retain homogeneity, and third the shaping of the gel prior to firing into the final product. (see Ref. 1 for details)

Mixing in Solution

Immediately after WWII the glasses and ceramics, the properties of which were the most accurately determined, were the laboratory samples used in phase equilibrium studies of the most significant ceramic systems. The arcane technique for making such samples had been developed and handed down through a succession of the most distinguished workers at the Geophysical Laboratory of the Carnegie Institution in Washington, DC. The names of N. L. Bowen, J. W. Greig, J. F. Schairer, G. W. Morey, E. F. Osborn, are familiar to all as the principal contributors to understanding the high temperature thermodynamics of the main ceramic oxide systems.(5) I was inducted into this tradition of preparing homogeneous glasses and ceramic powders therefrom as the first Ph.D. student of E.F. Osborn who had moved to Penn State in 1946 and set up the nation's second major center for phase equilibrium research. The Geophysical Laboratory process for making maximally homogeneous glasses and ceramics therefrom consisted of the melting of carefully weighed, well-mixed mixtures of oxides and carbonates of the composition desired, quenching to a glass, crushing to a fine powder in steel mortars, removing iron carefully with a magnet, and re-melting. It was necessary to repeat this entire process three to five times to achieve acceptable homogenization. I completed the determination of the equilibrium diagram of the system Li_2O_3-Al_2O_3-SiO_2 using this method to make homogeneous glasses and fine powders. Not only was it extremely tedious, but as I started to apply it to my own new <u>low</u> temperature phase equilibrium study — of the system Al_2O_3-SiO_2-H_2O (6) — two other major limitations of the melting to glass process came into focus:

First: The compositional range over which homogeneous glassy, thence crystalline, phase(s) could be obtained was quite narrow (e.g. in Al_2O_3-SiO_2 only compositions from 2 up to 15% Al_2O_3 could be retained as glasses).

Second: The structural bias introduced into these precursor glassy phases by the use of the high melting temperatures tended to favor a certain set of metastable products (in the case of Al_2O_3-SiO_2, those with Al in IV c.n.).

Moreover, using mixtures of the end members i.e. quartz and corundum, led to literally zero reaction in the p-t range involved. It thus became obvious that an alternative route to the preparation of chemically homogeneous glasses and other ceramic powders was desirable, and I therefore set about examining those methods which achieved homogeneity on an atomic scale by putting all the ions into solution. By chance, in a three- or four-year period starting July 1, 1948, out of this effort, we had developed three areas each of which has had a lasting impact on ceramic science: the sol-gel technique, new hydrothermal reaction techniques, and applications of phase separation in titania-rich glasses to glass-ceramics.

Relation to Colloid Science

The science of colloids or sols focused the attention of the chemistry community on this peculiar state of matter: a macroscopically homogeneous, "permanent"* suspension of solid particles in a liquid. Yet, in 1948, the bridges between colloid chemistry and ceramics were essentially zero outside the field of clay forming. None of the great colloid chemists--Zsigmondy, Svedberg, Freundlich(7-9) or their U.S. counterparts Weiser, Milligan, Hauser(10) got involved in anhydrous ceramic materials, although Weiser and Milligan worked extensively with oxide gels. Gels made the first link to ceramic technology via the patented methods for making SiO_2 and Al_2O_3 and TiO2 gels, including aerogels for various applications.(11 -12)

The next point of contact in applying colloid science to ceramics was in approaches to synthesizing clays.(13.14) Ewell and Insley made elaborate studies of co-precipitated (from sodium silicates and aluminum nitrates) gels of Al_2O_3 and SiO_2, purified by electrodialysis to remove Na as starting materials for kaolin synthesis. Raychaudhari and Dattu(15) published similar work on aluminosilicate and iron silicate precipitates from sols. A benchmark in the summary of research on sols and gels of silica and the silicates was R.K. Iler's "Baker Lectures" at Cornell.(2) Yet ceramics and glasses are hardly mentioned in the book, with the exception of the chemistry of synthesizing micas and clays (hydroxylated ceramic phases) via the SSG, route as noted above.

The first application of sol-gel methods for the production of chemically homogeneous anhydrous ceramics-bulk glasses in his case-appeared in a single paper by de Korosy(16) who also used the sodium aluminate-sodium silicate co-precipitation as the basis for making a gel precursor for glass.

Based on this background, our original efforts in 1948 were intended to make pure, anhydrous, homogeneous, crystalline and glassy one and multi-component ceramic phases. For the Al_2O_3-SiO_2 system it appeared possible, since one ion could be present as a cation and the other as an anion as Ewell and Insley(14) had already shown. That same process was also starting to be widely used in the technology of noncrystalline though anhydrous Al_2O_3-SiO_2 gel beads used as cracking catalysts. This was the method I first followed in trying to make homogeneous glasses in the system Li_2O-Al_2O_3-SiO_2, MgO-Al_2O_3-SiO_2, and found that with Na-salts as starting materials significant amounts of alkali and changes in Al/Si ratio were difficult to avoid. Even though I performed elaborate electrodialysis of the gels, purity and stoichiometry were problematic. Moreover, it soon became evident that neither could one obtain soluble salts of most high-

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*My friend, Professor Sir John Thomas, then President of the Royal Institution, showed me recently the vial containing a purple fluid, which was the gold sol prepared by Faraday himself well over 100 years before, and is still stable.

temperature oxides, nor was it possible to 'co-precipitate' all cations under the same Eh, pH conditions (not to mention the segregation 'via crystallization' problem during desiccation). It should be noted that in 1948 not a single stable oxide sol was available commercially. Ludox became available in the mid-fifties and we were one of DuPont's eager customers. Hence, the key innovation in establishing the solution-sol-gel process for making pure ceramic phases both glassy and crystalline was the author's introduction in 1949 of the more universal process *of using organometallics as sources of the major cations-e.g.* using ethyl orthosilicate and Al-isopropoxide in the Al_2O_3-SiO_2-H_2O study.(6) The method was successfully generalized to a three-component oxide system, MgO-Al_2O_3-SiO_2, by D.M. Roy and R. Roy.(17) Over the next decade this method for making precisely compositionally controlled glasses and ceramics was applied to virtually any composition even in 5-, 6- or 7-component systems by the author and his colleagues and students. The generalization proved so successful that dozens of graduate students started to use the "gel method" universally in the large number of mineral synthesis and phase equilibrium studies carried out in Penn State's geochemistry and ceramic technology departments in the fifties and sixties. A typical example of making the important ceramic phase, cordierite, ran as follows. The aliquot of prestandardized solution of TEOS in absolute alcohol was added to a solution made from the weighed amounts of the nitrates of Mg and Al dissolved in alcohol and water. This solution by adjusting pH and temperature (usually from 60°-90°C) gradually formed a sol and then, by appropriate temperature and time adjustment, a gel. This gel was desiccated to a xerogel, first on a water bath then typically at 500°-700°C. This yielded a noncrystalline solid (NCS) ultrafine, chemically pure powder of the cordierite or any other chosen composition. Such powders in our work were typically and routinely (a) melted to glass, (b) hydrothermally crystallized to fine hydrous or anhydrous, low temperature ceramic powders with a high degree of structural order unattainable by any other process, (c) crystallized dry to a ceramic aggregate (though *not* as a *shaped desired product).*

Starting in 1951, our work on systematic phase equilibria began to include the titanates and niobates, and the sol-gel method was further generalized in a wide variety of papers. As a source for Ti we used both $TiCl_4$ and titanium-butoxide in many cases, e.g. in the systems TiO_2-SiO_2,(18) BaO-TiO_2-SiO_2,(19) BaO-CaO-TiO_2-SiO_2,(20) etc. Many of these early oxide powders or xero-gels were used in "hydrothermal" work as reactive starting materials and the author's first brief review on the sol-gel process carried this connection in the title.(21) The goal which was a process for making nanoscale (in today's terminology) ultrapure, stoichiometric ceramic powders of virtually any composition had been reached. The title of my first review "Methods of making mixtures for both dry and wet phase equilibrium studies," accurately points to the goal we had achieved: Pure reactive ceramic precursors for scientific research, and that is where the major impact has been. This paper on the sol-gel process became the first Citation Classic in the field of ceramics and the first citation classic ever published (Fig. 1) in the *Journal of the American Ceramic Society,* showing objectively its impact on the field by 1987.

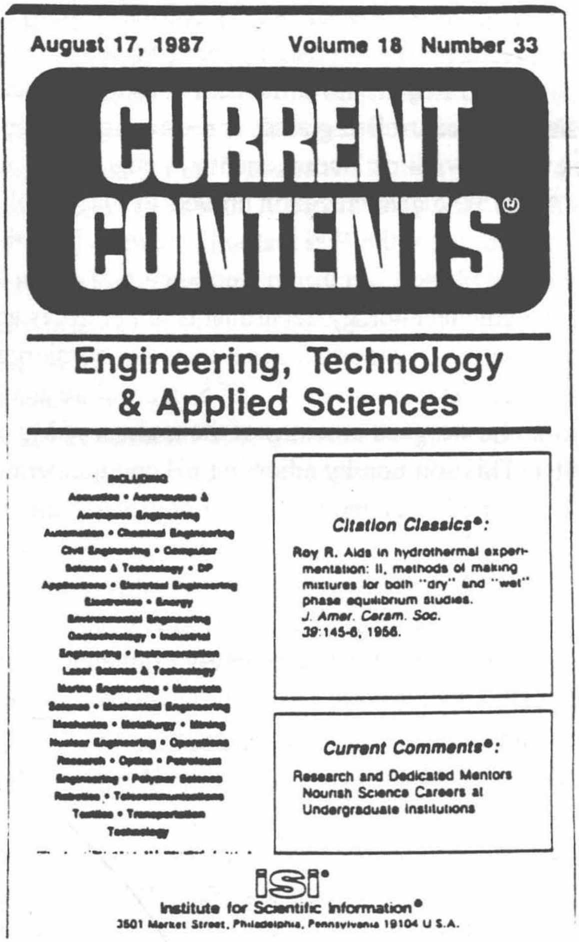

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Figure 1: Cover of Current Contents issue, which records the fact that the original sol-gel article in the Journal of the American Ceramic Society, had been cited so frequently that it had attained the status of "Citation Classic." It was the first ever in that Journal and the first in the field of ceramics.