The Sol-Gel Process for the Synthesis and Processing of Ceramic Powders

H. Schmidt

1 Introduction

The sol-gel process represents a method for the synthesis of non-metallic-inorganic materials like glasses and ceramics. It is based on a chemical condensation reaction starting from molecular or colloidal precursors. In general, through the following condensation reaction (eq. 1)

$$\equiv MeOH + xMe\equiv \rightarrow \equiv Me\text{-}O\text{-}Me\equiv \quad (1)$$

which can take place between reactive molecules or surfaces of colloids, particles in the range of some nanometers up to micrometers can be formed. The initiation reaction of the small particles follows the rules of nucleation and growth from solution. By controlling the reaction conditions (precursor concentration, solvent temperature), very low particle sizes can be obtained [1]. As precursors, a wide range of soluble compounds (oxides, sols, hydroxides, complex ions or alkoxides) can be used, and a variety of compositions can be synthesized including multicomponent and doped systems, functional ceramics and structural ceramics. The process is mainly restricted to oxidic systems. Non-oxide systems are much more difficult to prepare.

In order to avoid precipitation, the colloidal systems have to be stabilized, which normally is carried out by generating electric charges (e.g. by establishing the proper pH value) on the particle surface. Due to the small particle size, the solid contents of electrostatically stabilized sols are comparatively low (around 10 vol-% depending on the system) which normally does not allow conventional ceramic processing. Destabilization of sols leads to coagulation and the formation of gels. Powders can be obtained by grinding gels followed by calcination if densified or crystalline powders are required.

2 Material Developments

Based on the synthesis principles described, a variety of ceramic materials can be developed. One of the possibilities is the tailoring of intermediates before solidification to gels with adjusted viscosity for coating and fiber drawing processes. Another is the fabrication of finely divided high-performance ceramic powders for conventional processing. A third possibility is the use of colloidal systems to form thin porous coatings for membranes or to use them as inorganic binders in conventional ceramic processing.

2.1 Coatings and Films

Based on the reaction principle, colloidal systems having very low viscosities can be prepared to be used for thin films [2]. Coatings from a variety of systems (ZrO_2, Al_2O_3, SiO_2, $BaTiO_3$, PZT, $LiNbO_3$) were prepared. These coatings were applied by dipping or spin coating and densified to crystalline films at temperatures substantially lower than those used in conventional powder processing. For example, lithium niobate films can be obtained as single crystals on a variety of substrates at 300°C which is based on the unique possibility to tailor structures already close to the final structure in the solution [3]. Similar examples have been shown with barium titanate or PZT [4]. Recently, large-scale applications were demonstrated by *Nisshin Steel Company* (Japan) using the sol-gel process for large-scale stainless steel coating with SiO_2 [5]. Zirconia is another interesting candidate for the coating of steel.

Another type of coating is the alumina coating on cordierite as a support for platinum for application in automotive catalysts. Ceramic film formation processes have been developed by *Mitsubishi* (Japan) allowing the fabrication of free-standing aluminum foils from 3 to 100 µm thickness for electronic substrates and acoustic membranes [6]. Ceramic coating techniques on flat glass have been developed by *Schott Glass* (Germany) (e.g. TiO_2, TiO_2/SiO_2, indium oxide, etc.). Ceramic membranes with coatings of about 1 µm of thickness and with high separation performances from zirconia, alumina, spinels, etc. have been developed [7, 8] which already are applied very successfully in industry.

These few examples show the large potential for sol-gel ceramic coatings which is by far not exploited completely. Future activities of increasing interest will be in the field of functional coatings (electrochromic devices based on tungsten oxide, semi-conductive coatings for selective light transmission, electroceramic films for optical light processing, protective coatings on metals, functional coatings on glass).

2.2 Fibers

The same basic principles required for coatings can be used for drawing ceramic fibers. For this reason, the rheological properties of sols for fiber drawing have to be tailored. This can be done either by adding additives like organic polymers or by tailoring the particle-to-particle interaction in a way that the desired properties are established. For the surface interaction control, organic additives deposited on the surface are very effective, as shown, for example for the fiber drawing of alumina [9]. A variety of fiber drawing processes based on sol-gel techniques have already been commercialized successfully [10]. These fibers are based mainly on alumina or composites like Al_2O_3/SiO_2, or $SiO_2/BaTiO_3$ or Nextel fibers. SiO_2 fibers have been developed by *Asahi Glass* (Japan) and commercialized successfully, too. Future developments with respect to fibers will focus on functional fibers like high-T_c superconductors, PZT or barium titanate. Another interesting example is IR-transmitting fibers. In this case, however, technology is rather difficult.

2.3 Powder Preparation

Fabrication of ceramic powders by sol-gel processes seems to be the easiest task, but whereas the preparation step of sols and gels is rather simple, the processing of these powders can become very challenging. In order to maintain the high sintering activity of small-particle powders, it is necessary to process them to high-solid-content systems which requires very special techniques. A variety of powders synthesized by the sol-gel process are now available, for example, barium titanate by *DuPont* (USA) or zirconia by *Sumitomo Chemicals* (Japan). An interesting development has been made by *Norton* (USA) and *3M* (USA) company, developing grinding powders based on alumina with ultra-high performance. This development is based on the fact that the microstructure of alumina produced from gels can be tailored by a well-defined number of added nuclei of α-alumina (seeding).

For ceramic powders, the sol-gel process offers a very interesting potential, but the price/performance ratio has to be taken into consideration. The exploitation of the potential requires new processing techniques if the intrinsic high sintering activity of these powders is to be converted into technical production. For the future, the production of low-cost, high-performance nano powders is of great interest.

3 Processing – Consideration and Nanotechnologies

Ceramic intermediates fabricated by the sol-gel process not only have an interesting potential to be processed to materials, but to use them as processing aids. This may be of great interest for a homogeneous distribution of additives in a powder system, e.g. for the fabrication of zinc oxide varistors or addition of additives in wet processing. In this case, the additive can be prepared as a colloidal sol with nanoscale particles and by tailoring the electric charges of the ceramic powders (they have to have the opposite charge of the sol particles), the sol particles can be deposited on top of the ceramic powder. This powder coating technique allows the fabrication of high-performance ceramic raw materials with excellent sintering properties. In Fig. 1, the principle is demonstated schematically.

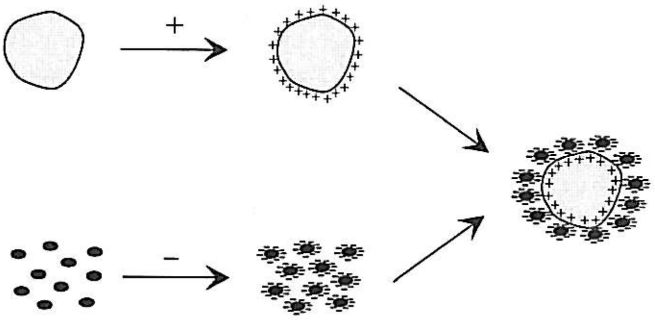

Fig. 1 Schematic diagram of the preparation of ceramic powder with deposited additives using sol-gel techniques

This type of sol-gel processing can also be considered as a colloidal-assisted ceramic powder processing. As recently shown, using this technique, silicon carbide can be densified pressurelessly to almost theoretical density at 2000°C using conventional ceramic SiC powders [11]. In combination with the surface tailoring of the main-component ceramic powder by chemical surface modification (Fig. 2), these principles represent a basic strategy for fabrication of tailor-made ceramic powders with improved performance for the production of ceramic parts, especially with high-pressure slip casting, where segregation can be prevented completely.

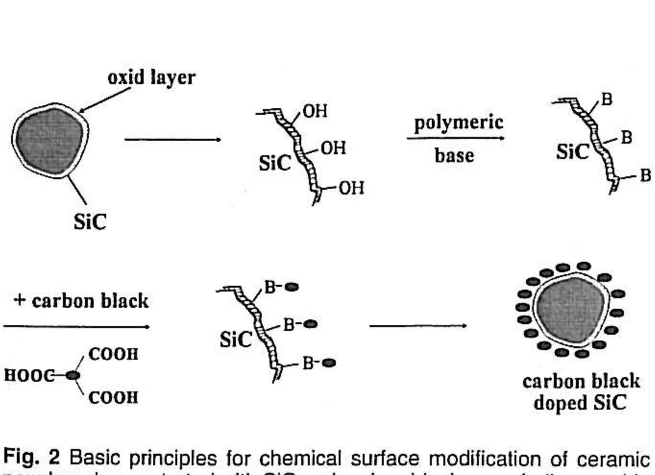

Fig. 2 Basic principles for chemical surface modification of ceramic powders demonstrated with SiC and carbon black as an indispensable sintering aid (Figs.: INM)

This tailored surface modification, especially if short-chain organic molecules are used, makes it possible to process nano powders to high green densities if the modifiers are selected to control particle-to-particle interaction. As shown in the example of alumina (boehmite, particle size: 15 nm), it is possible to obtain green densities as high as 65 vol-% without any agglomeration. Similar results have been obtained with nano-scale titanium nitride [12, 13]. In the latter case, titanium nitride could be densified at 1050°C to full density compared to over 2000°C with µm particle size. In connection with tape or gel casting, nano particles can act as binders, replacing organic systems to a great extent.

These examples show how sol-gel techniques can be used for processing and nanoprocessing ceramics. Nanoprocessing in particular offers a very interesting potential due to the low sintering temperatures. As already found during densification process, almost no grain growth is observed, so that dense nano-scale ceramics are obtained. By further heating at higher temperatures, grain growth to a desired level can be initiated. This leads to an interesting concept of separating densification and microstructure formation, leading to the idea of defect-free ceramics for structural as well as functional ceramics.

Institut für Neue Materialien gem. GmbH, Im Stadtwald, Gebäude 43, D-66123 Saarbrücken, Germany

References

1. E. Matijevic: Preparation and Interactions of Colloids of Interest in Ceramics. Ultrastructure Processing of Advanced Ceramics. J.D. Mackenzie, D.R. Ulrich (Eds.), John Wiley & Sons, New York (1988) 429
2. D.R. Uhlmann, G.P. Rajendran: Coatings: the Land of Opportunity for Sol-Gel Technology. Ultrastructure Processing of Advanced Ceramics. J.D. Mackenzie, D.R. Ulrich (Eds.), John Wiley & Sons, New York (1988) 241
3. S. Hirano: Novel Route for In-Situ Control of Ceramic Microstructure. Proceedings of the International Symposium on Molecular Level Designing of Ceramics, Team on the NEDO International Joint Research Program (Ed.), Nagoya (1991) 77
4. E. Wu, K.C. Chen, J.D. Mackenzie: Ferroelectric Ceramics - the Sol-Gel Method versus Conventional Processing. Mat. Res. Soc. Symp. Proc. **32** (1984) 169
5. K. Izumi, N. Minami, Y. Uchida: Sol-Gel-Derived Coatings on Steel Sheets. Proc. of 1st Int Conf. on Application and Commercialisation of Sol-Gel Processing, Saarbrücken, Oct. 10-13, 1993, Trans Tech Publications Ltd., Aldermannsdorf, Switzerland (in print)
6. M. Ono: Sol-Gel Processing of Advanced Ceramics for Electronic Applications. Ceramic Powder Processing Science, H. Hausner, G.L. Messing, S. Hirano (Eds.), Deutsche Keramische Gesellschaft e.V., Cologne (1989) 35
7. C. Guizard, A. Julbe, A. Larbot, L. Cot: Oncoming Developments on Sol-Gel-Derived Membranes. Proc. Eurogel 91 - Progress in Research and Development of Processes and Products from Sols and Gels. S. Vilminot, R. Naß, H. Schmidt (Eds.), North Holland Publishers, Amsterdam (1992) 167
8. H. Chmiel, V. Mavrov: Requirements and Materials for Higher Selective Separation in Process Integrated Environmental Protection. Extended Abstracts of the Third Saar-Lor-Lux Meeting on Tailoring of Materials for Industrial Applications. Centre de Recherche Public, Centre Universitaire, Luxembourg, (Ed.) December (1993)
9. German Patent (Offenlegungsschrift) DE 41 16 523 A1: Verfahren zur Herstellung von a-Al_2O_3, May 21, 1991
10. L.C. Klein (Ed.): Sol-Gel Technology for Thin Films, Fibers, Preforms, Electronics and Speciality Shapes. Noyes Publications, Park Ridge, New Jersey, 1988
11. R. Naß, M. Aslan, R. Nonninger, H. Schmidt: Neue Konzepte zur Herstellung von entmischungsstabilen Gießschlickern im System SiC/B_4C/C. cfi/Ber. DKG (in print)
12. R. Naß, S. Albayrak, M. Aslan: Synthesis and Processing of TiN-Coatings. Extended Abstracts of the Third Saar-Lor-Lux Meeting on Tailoring of Materials for Industrial Applications. Ed.: Centre de Recherche Public, Centre Universitaire, Luxembourg, December (1993)
13. H. Schmidt, R. Naß, M. Aslan, K.P. Schmitt, T. Benthlen, S. Albayrak: Synthesis and Processing of Nanoscaled Ceramics by Chemical Routes. J. de Physique IV, Colloque C7, supplément au Journal de Physique III **3** (1993) 1251 ❑