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"Oxide Ceramic Alloys and Microlaminates" (1996-1999)
and
"Low Temperature Processing and Kinetics of Ceramics and Ceramic Matrix
Composites with Large Interfacial Areas" (1999-2000)

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We have discovered a novel two-step sintering method that opened up a low temperature processing window within which fully dense nanocrystalline yttrium oxide was obtained. The success of this method contradicts the classical sintering paradigm, in that there is no concurrent grain growth during final stage sintering. This advance could significantly simplify the task of obtaining dense nanocrystalline ceramics and composites. We have developed a new method of processing laminate ceramics using deformation processing in the green state. By adjusting the deformation resistance of the constituent slurries, two phase laminates with different interfaces, from planar to wavy, have been obtained. These ceramics show improved sintering characteristics and the fired ceramics exhibit high strength and toughness. We have lastly developed a colloidal processing technique to encapsulate biomolecules at ambient, neutral-pH, aqueous conditions. The gelled composites are transparent and bioactive, and the biomolecules contained have improved thermal and chemical stability and exhibit enhanced biofunctionality in redox reactions.

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The grants supported research on CeO_2 and Y_2O_3 sintering, microlaminates of Ce-TZP/ Al_2O_3 (Ce-TZP stands for CeO_2 -stabilized Tetragonal Zirconia Polycrystal, which transforms profusely under stress into the monoclinic phase) and Y-TZP/porous Al_2O_3 (Y stands for Y_2O_3), and a new initiative in 1999 on organic/inorganic nanocomposites. Major accomplishments in the above period are summarized below.

1 Sintering of fine ceramic oxide powders

Fine powders have been regarded as an important step toward achieving superior sintering performance and nanograin ceramics. In reality, however, the experience of researchers on these powders varies and it does not always lend support to the above expectation. Agglomeration, often severe for fine powders, has been thought to be the main problem. In addition, rapid coarsening of the fine powders during sintering is thought to remove much of their advantage. We have undertaken a study to attempt to determine the microstructure evolution of fine powders during sintering in order to gain a better understanding of their sintering behavior.

We have prepared fine powders of CeO_2 and Y_2O_3 for sintering studies. These powders are structurally related to nuclear materials such as UO_2 , PuO_2 , ThO_2 , and ZrO_2 , and they all have a wide range of solubility for various cations making them a suitable host material for incorporating nuclear waste. These oxides are cubic, their diffusion controlled by cations via an interstitial mechanism, and their grain boundary mobilities have been determined as a function of temperature and dopant types. These powders have excellent sinterability, as evidenced by the very low sintering temperature achieved (less than 0.45 of their respective melting points of the oxides). In addition, we have shown that green compacts with a relative density as low as 18% could be sintered to full density. Thus, one might assume that these powders do not suffer from hard agglomeration.

Sintering and microstructure data obtained have allowed us to establish the following conclusions.

(a) Universal Pore Structure--We have shown that the normalized pore size (pore size divided by the particle or grain size) follows a universal correlation with the density (ranging from 18% to 80%). A simple packing model was constructed to provide an analytical prediction for the normalized pore size that agrees with the experimental data.

(b) Critical Pore Size--According to Kingery and Francois, there is a critical pore size, beyond which pores should grow whereas below which pores should shrink. This concept is analogous to the one of critical grain size in grain growth and is based on equilibrium considerations of grain boundary energies and surface energies. (In amorphous matter, there is no critical pore size in sintering. Thus, this is a fundamental concept that makes sintering of crystalline matter thermodynamically different from sintering of amorphous matter.) Despite much reference to the concept since it was proposed in 1960s, it has not been quantitatively verified by experiment. From normalized pore size distributions, we have determined that the critical pore size in both CeO_2 and Y_2O_3 is about 0.5 of the particle size. This value is independent of the density, as expected from the thermodynamic nature of the concept, and its magnitude is consistent with the value predicted from the measured dihedral angle (around 110° in both materials.)

While the above two findings are probably general and are a direct application of the classical concept of sintering, the following two findings are novel and not at all expected from the conventional sintering theory. They are also believed to be unique to fine powder compacts.

(a) New Sintering Mechanism--According to the universal correlation between normalized pore size and density that we established, the majority of pores in compacts of less than 65% relative density are supercritical for CeO_2 and Y_2O_3 . Therefore, they do not have the positive driving force for pore filling. Yet, experimentally, we have found compacts of much lower density have no difficulty in densification. A new sintering mechanism is thus needed to explain the sintering behavior for densities as low as 18% to about 65%, namely the so-called initial stage in the conventional classification of sintering stages. The new sintering mechanism we proposed is a particle-rearrangement mechanism triggered by particle coarsening that motivates repacking of particles to a higher density. (In the conventional sintering theory, particle-rearrangement is indeed regarded as the most important mechanism; but it is for liquid phase sintering and not for solid state sintering.) For fine powders, our experimental results strongly suggest that particle-rearrangement (or particle-group rearrangement) must be operating. In this mechanism, there is no pore filling by diffusional transport, but surface diffusion is important since it controls the kinetics of particle coarsening. Inasmuch as coarsening is a necessary step in the above

picture, this sintering mechanism is active only if coarsening is active, namely in fine powder compacts.

Coarsening has been previously proposed to be beneficial to sintering because, for a given pore size, a coarsened particle size pushes up the critical pore size so that more pores become subcritical and hence sinterable. At lower compact densities this scenario is not realistic for the majority of pores, since the ratio of pore size to particle size increases rapidly at lower densities. (Fine powders tend to achieve a lower packing density in the green compact because of the stronger surface forces.) For these compacts, the rearrangement mechanism that we envisage seems more appropriate. For these powders, coarsening is a natural course and coarsening-motivated particle rearrangement seems to be the most efficient way for them to improve the density in the initial stage sintering. This ability to coarsen and to improve packing density is a unique feature of fine powders.

(b) Two-Step Sintering--According to conventional sintering theory, pore channels are effective in arresting grain growth, but as the pore channels collapse via Rayleigh instability into isolated pores the grains begin to grow and this retards sintering. A local density of about 92% is required for the breakdown of pore channels in a polycrystalline ceramics with a typical dihedral angle. Thus, grain growth is commonly observed in the final stage sintering starting from 85% to 93% depending on the uniformity of local density. Contrary to this general experience, we found it was possible to arrest grain growth even in the final stage sintering. We achieve this by first fast firing powder compacts to a density higher than the critical one that renders all pores subcritical. This density is typically about 75% in CeO_2 and Y_2O_3 . The compact is then cooled and resintered at a lower temperature. Although the sintering rate in the second stage is slower, it is still driven by the same positive driving force and it can proceed until the full density is reached. Remarkably, the grain size remains constant throughout this process and does not even grow after full density is reached. By two-step sintering, we have obtained fully dense Y_2O_3 at 800°C and CeO_2 at 600°C, with a grain size from 60 nm to 300 nm.

Sintering without grain growth has been commonly obtained by hot pressing. This is because the mechanical force provides an additional driving force for densification but not for grain growth. Yet in our two-step sintering experiments the driving force was not altered and is provided by the capillary force of surface energy or grain boundary energy.

Therefore, there is no energetic argument that can explain final stage sintering without grain growth. This suggests that the kinetics of sintering and grain growth are not parallel (both controlled by grain boundary diffusion) as is often thought to be the case for fine grain ceramics. One possibility is that the triple point mobility is severely hampered at low temperature, and it causes the arrest of grain growth in a very fine grain microstructure.

The work on sintering of fine oxide powders was documented in two papers published in *Journal of the American Ceramic Society*. The work on two-step sintering was documented in one paper published in *Nature*.

2 Laminar and cellular composites

Layered ceramic composites are currently used in fuel cells, capacitors, and varistors, as well as in some high-performance applications such as structural ceramic parts. As structural materials, layered composites possess outstanding mechanical properties. Two types of structural composites can be distinguished for structural applications. First, a strong interface between two constituent phases is present to permit load transfer and deformation or phase transformation to occur in the tougher phase. This applies to ceramic/metal or ceramic/polymer composites, but it also applies to $\text{Al}_2\text{O}_3/\text{Ce-TZP}$ composites where Ce-TZP undergoes stress-assisted transformation. In the second type of composites, a weak interface is present which allows crack deflection and crack arrest to occur. This, for example, is the case in SiC/C layer composites. Processing of these composites usually relies upon hot pressing. In addition, the microstructure of the composite is limited to parallel stacking of flat layers. As a result, the materials are highly anisotropic and weak under transverse loading conditions. On the other hand, while a variety of periodic microstructures have been obtained by the use of fibrous monolith techniques, such techniques again depend on hot pressing when structural ceramic parts are involved.

An examination of fracture patterns of the layered composites suggests that the fracture process zone size in many cases is of the order of tens to hundreds of microns. Theoretically, if the coherence length of the layer exceeds the process zone size, then very similar mechanical properties should be obtained. Indeed, much beyond a length scale of the process zone, the layer may well be discontinuous. Furthermore, although the

alignment of fiber direction is known to be critical for fiber-reinforced polymer matrix composites to withstand buckling, buckling is not a serious problem for ceramic/ceramic composites which do not have an elastically soft matrix. Thus, even if the layers have some curvature, they should still have essentially the same mechanical function as flat-layer composites. We therefore expect composites with a microstructure containing discontinuous and curved layers to deliver good mechanical performance. This should be obvious by viewing the typical microstructure of a wood panel; layers are indeed curved and have only finite coherent length, yet wood has rather good mechanical properties.

We have developed a novel processing method to create a wood-like microstructure containing discontinuous and curved layers of ceramics. (In the following, we refer to this type of microstructure as cellular to differentiate it from the conventional one of flat layers, which we will refer to as laminar.) In fact, the method allows a continuous transition of the microstructure from laminar to cellular. In this process, we roll or otherwise deform a plastic bilayer ceramic sheet to reduce the thickness. After that, we fold the sheet over itself and repeat the process. As the process continues, the number of layers doubles with each folding. If the total thickness of the sheet is maintained constant by deformation, then the thickness of the layer after N foldings is 2^{-N} of the original. This method can be carried out using either dense aqueous slurries without any plasticizers or binders, or using conventional tape casting with plasticizers and binders. To induce the microstructure transition, the key parameter that we exploit is the ratio of the flow stress (or the viscosity) of the two layers. When they are well matched, the layers remain planar even after many foldings and much deformation. When the ratio is far from unity, the layers become curved and later break down, mixing the two phases. With further deformation, the rheologically harder phase always become entrapped in the matrix of the rheologically softer phase. Mechanically, the former may be considered to undergo a necking process in the surrounding of the latter. For aqueous slurries, we can adjust the rheology by the content of the salt and monitor it by the viscosity; the greater the salt content, the harder the slurry. For slurries with plasticizers and binders, we can adjust the rheology by the composition of the organics and monitor it by the softening temperature; the higher the softening temperature, the harder the slurry. The final microstructure of the cellular composite is rather similar to that of a wood.

Dense $\text{Al}_2\text{O}_3/\text{Ce-TZP}$ composites with either a laminar or a cellular microstructure have been obtained. These composites have a strong interface and the presence of Al_2O_3 deflects the propagation of the stress-assisted transformation in the TZP region. The microstructure transition occurs at large deformation after many foldings, and the number of foldings required to reach the transition is controlled by the ratio of the flow stresses of the two layers. Meanwhile, the thickness of the layer continues to decrease. These composites show a strong correlation between sinterability, mechanical properties and the connectivity of the microstructure. Sintering rate is anisotropic in all the laminar composites but such anisotropy disappears when the laminar microstructure transforms to a cellular microstructure. Meanwhile, the strength of the composite increases with decreasing thickness, most especially after the transition. Such an increase in strength, reaching 1 GPa, is accompanied by an increase in the amount of transformation in the zirconia layer. The composites also exhibit extended *R*-curve behavior, with the toughness reaching beyond $15 \text{ MPa}\cdot\text{m}^{1/2}$; meanwhile, the steepness of the *R*-curve also increases after the transition. Apparently, the composites benefit not only from the more extended transformation zones that are spread out normal to the crack plane, but also from crack deflection and branching. This observation that both the strength and the amount of transformation increase monotonically with decreasing layer thickness is rather unusual for zirconia-alumina composites, since particulate composites of similar compositions usually show an opposite trend with the dispersed alumina suppressing the transformation. This suggests that the shape of the alumina phase is important, one with a high aspect ratio (typically 100 or so in our material) being the most desirable. Essentially, when the alumina phase has a shape of a pancake, its edge serves as the site of many effective stress concentrators that trigger the phase transformation in the zirconia phase. As the layer thickness becomes thinner, the volume density of such stress concentrators increases so the amount of transformation and strength increase.

Laminar/cellular composites with weak interfaces have also been obtained using the alumina/zirconia system using slightly different formulations. For such composites, at least one constituent phase should have a high strength. In our design, we have chosen Y-TZP as the strong phase and porous alumina as the weak phase, in the latter the porosity is controlled by using either a fugitive additive (various starches, and an alkaline soluble

swellable polymer) or a powder that has a poorer sinterability. The transition from a laminar to a cellular microstructure has again been observed. Both laminar and cellular composites exhibit crack branching and deflection during extended post peak-load deformation (i.e., a graceful failure.) Our analysis suggests that the residual stress is important in this system and can be beneficial for inducing crack branching and deflection at the interface. This mechanism favors laminar composites but it is still preserved in cellular microstructures.

The results of Ce-TZP/ Al_2O_3 composites with a strong interface are described in three papers in *Journal of the American Ceramic Society*. The results on Y-TZP/ Al_2O_3 composites with weak interfaces have been reported in a paper published in *Journal of the American Ceramic Society* and a manuscript submitted to *Zeitschrift fur Metallkunde*.

3 Inorganic/Organic Nanocomposites

A large variety of inorganic-organic hybrid materials have been investigated in recent years. For example, the bio-inspired synthesis of hybrid materials aims to replicate the intricate microstructures of many natural living materials that have impressive strength and toughness. Other hybrid materials aim to combine the merit of inorganic and organic materials. For example, polymer filled sol-gel glasses retain the transparency of the aerogel, but have much higher toughness than glass and much higher hardness than polymers. Such materials may be used as low-density, high impact-toughness windows. Likewise, polymers polymerized in the presence of many mica sheets are processable as polymers but have much improved thermal stability, allowing them to be used as hot parts in automobiles and aerospace structures. Biosensors have also been prepared by encapsulating proteins and other biopolymers in a transparent sol-gel glass. The proteins are immobilized but they retain their biofunctions, reacting with incoming ions or solutions that diffuse through the porous matrix. Such reactions are often readily detectable by the change in the optical absorption resulting in a change of color. Therefore, these composites can be used as biosensors for gas and liquid species. A similar class of hybrid composites incorporating enzymes and other biopolymers can be used for bioreactors for energy generation and other reactions. Note also that a significant part of the above work is based on the use of sol-gel methods to prepare the inorganic matrix. This is not surprising since

the sol-gel method is a well-established route to obtain inorganic monoliths at low temperatures. Furthermore, of the work based on the sol-gel method, nearly all of it is silica-based and uses alkoxides which require the addition or release of alcohol in the course of the preparation. Unfortunately, the presence of alcohol can cause denaturalization of many biopolymers (causing chain unfolding or molecule aggregation), so the types of biopolymers that can be incorporated in these composites are thus far severely limited.

We have prepared inorganic/organic hybrid composites using biopolymers and sol-gel techniques that are aqueous based and are entirely free of alcohol. Essentially, stock solutions are first prepared to contain a high concentration of silica sols, and the biopolymers such as proteins are then introduced. Subsequent gelation takes place over time under a suitable chemical condition, often in a biopolymer-compatible buffer solution to limit the change of the pH value. The gelation process can be controlled to obtain different viscosities so that the liquid can be shaped into a monolith or a thin film. After drying, a transparent monolith or a thin film can be obtained. Since the sols obtained in our method have a diameter of only several nanometers, the pore space between them is very fine and is entirely adequate for immobilizing typical biopolymers of large molecular weights. Meanwhile the pore space still allows smaller ions and solutions to penetrate. Optical absorption spectroscopy has verified that the proteins are completely active after encapsulation, as their characteristic absorption band shows no shift in energy nor decrease in absorbance at any stage of the hybrid preparation. Thus, the technique appears suitable for encapsulating any biopolymer or enzyme. We believe this is but one method that can be used to prepare inorganic/organic nanocomposites without alcohol.

The proteins encapsulated in colloidal silica without alcohol show better activity and structural stability than either the unencapsulated proteins or proteins encapsulated in alkoxide gels. The host matrix also protects proteins from denaturation in harsh environments such as high heat (up to 80°C), strong acid (pH3) or base (pH11) conditions. This stability can be optimized further by controlling the processing time, and the size and volume fraction of the colloidal silica particle. The shorter the gelation time and the smaller the colloidal particle size, the better the stability. We believe that one main reason for protein denaturation in the surrounding of oxide particles is the strong tendency for

proteins to absorb onto the oxide surface. A short gelation time and the small interstitial size restrict the mobility of the proteins so that they can not reconfigure and absorb.

The initial results of this research are described in a paper published in *Acta Materialia*. Several other presentations were made in the meetings of Materials Research Society and American Ceramic Society in Spring 2000. A patent application has been filed to the US Patent and Trade Office.

4 Publications

"Grain Boundary Mobility in Y_2O_3 : Defect Mechanism and Dopant Effects," P.L. Chen and I-Wei Chen, *J. Am. Ceram. Soc.*, 79 [7] 1801-09 (1996).

"Grain Growth in CeO_2 : Dopant Effects, Defect Mechanism, and Solute Drag," P.L. Chen and I-Wei Chen, *J. Am. Ceram. Soc.*, 79 [7] 1793-800 (1996).

"Sintering of Fine Oxide Powders: I. Microstructural Evolution," P.L. Chen and I-Wei Chen, *J. Am. Ceram. Soc.*, 79 [12] 3129-41 (1996).

"Sintering of Fine Oxide Powders: II. Sintering Mechanisms," P.L. Chen and I-Wei Chen, *J. Am. Ceram. Soc.*, 80 [3] 637-45 (1997).

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"Solution Mechanisms for Dopant Oxides in Yttria," G. Busker, A. Chroneos, and Robin W. Grimes, *J. Am. Ceram. Soc.*, 82 [6] 1553-59 (1999).

"Bimaterial Composites via Colloidal Rolling Techniques, I. Microstructure Evolution during Rolling," M. Menon and I-Wei Chen, *J. Am. Ceram. Soc.*, 82 [12] 3413-21 (1999).

"Bimaterial Composites via Colloidal Rolling Techniques, II. Sintering Behavior and Thermal Stresses," M. Menon and I-Wei Chen, *J. Am. Ceram. Soc.*, 82 [12] 3422-29 (1999).

"Bimaterial Composites via Colloidal Rolling Techniques, III. Mechanical Properties," M. Menon and I-Wei Chen, *J. Am. Ceram. Soc.*, 82 [12] 3430-40 (1999).

"Encapsulation of Protein Molecules in Transparent Porous Silica Matrices via an Aqueous Colloidal Sol-gel Process," D-M. Liu and I-Wei Chen, *Acta Mater.* 47 [18] 4535-44 (1999).

"Sintering Dense Nanocrystalline Ceramics without Grain Growth," I-Wei Chen and X-H. Wang, *Nature*, 404, 168-71 (2000).

"Crack Deflection in Composites with very Thin Interlayers," E. J. Winn and I-Wei Chen, *J. Am. Ceram. Soc.* 83 [12] 3222-24 (2000).

"Grain Boundary Kinetics in Oxide Ceramics with the Cubic Fluorite Crystal Structure and its Derivatives", I-Wei Chen, *Interface Sci.* 8, 147-156 (2000).

"Application of Deformation Instability to Microstructural Control in Multilayer Ceramic Composites," I-Wei Chen, E.J. Winn, and M. Menon, accepted for publication in *Mater. Sci. & Eng. A*, special issue for A. S. Argon Symposium.

"Delaminating Oxide Layer Composites with Wavy Interfaces," submitted to *Z. Metallk.*, invited contribution to the special issue for G. Petzow.