

Volume 1, Numbers 1 and 2, 1994

INTERNATIONAL CERAMIC MONOGRAPHS



Proceedings of the International Ceramics Conference
Austceram 94

25-27 July 1994
Sydney, Australia

Edited by C.C. Sorrell and A.J. Ruys

Australasian Ceramic Society
Sydney

THE USE OF COLLOIDAL AND SURFACE CHEMISTRY FOR PROCESSING NANOSIZED CERAMIC POWDERS

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THE USE OF COLLOIDAL AND SURFACE CHEMISTRY FOR PRO- CESSING NANO-SIZED CERAMIC POWDERS

1. ABSTRACT

Surface and colloidal chemistry have been applied to the synthesis and processing of nano-scale ceramic powders. Redispersible oxides, e.g. ZrO_2 and Y_2O_3/ZrO_2 with particle sizes less than 20 nm have been prepared by the microemulsion technique as well as by thermodynamically controlled growth reaction in the presence of surface active compounds. By surface modification with short-chained organic molecules which provided short-range steric repulsive forces, nano-scale boehmite and TiN could be processed to high green density compacts. Due to the small particle size of TiN (40 nm) and homogeneous green microstructure, nearly full density (> 98 %) was achieved below 1300 °C with neglectable grain growth. The system SiC/B₄C/C has been investigated for the improvement of the carbon black distribution within the green specimens prepared by casting techniques and electrophoresis, respectively. For slip casting it was found that nano-scale carbon black can be directly deposited on the surface on the SiC-particles which leads to significantly improved processing and properties of the sintered material ($T_B > 600$ MPa, $HV_{05} = 31$ GPa). An excellent sintering aid distribution within the green parts was achieved by electrophoresis after careful adjustment of the electrophoretic velocity of the different components by surface modification with a polymeric base.

2. INTRODUCTION

Wet processing of ceramics is a very old technology developed on the basis of clay minerals which have the ability to undergo a plastic deformation during the processing step like mechanical forming or extrusion. This ability is based on intrinsic properties of clay minerals like

caolinite or montmorillonite and the basis of silicate ceramic technologies. Other oxide or non-oxide ceramic systems, in general, do not show these properties. In this case, for processing other routes have to be used. To introduce plasticity, for example for ceramic injection moulding (CIM), plastifying additives like polymers are widely used [1]. Independent of the type of processing, there is one common target: to reduce defect rates and to obtain green bodies as homogeneously as possible and to end up with high green densities. To achieve these goals with wet processing techniques like slip casting, additives have to be used to reduce the particle-to-particle interaction and to obtain high slip densities at low viscosities. For this reason, the control of particle-to-particle interaction is one of the most important parameters in ceramic wet processing, and in general, the interaction is controlled by electric charges, generating repulsion forces between the particles. Electric charges on particle surfaces, for example, can be generated by ion adsorption. For this reason, ionic additives are used. If the ions are based on organic compounds, an additional effect is added which is known as electrosteric surface modification [2].

As long as particle sizes are in the micrometer or in the upper submicrometer range, the "volume" added by the adsorption of these additives (the volume of the adsorbed species including the "volume" caused by electric charges) on the particle surface is not significant since this volume only adds „shells“ in the nanometer range to the particle. With decreasing particle size, however, the volume fraction added by adsorption is increasing and thus, the solid content of the slip is decreasing. If particle sizes in the lower nanometer range are considered, the absorbed volume reaches the order of magnitude of the particle volume and can even be higher. In fig. 1, the relationship between particle size, particle distance and solid content is shown.

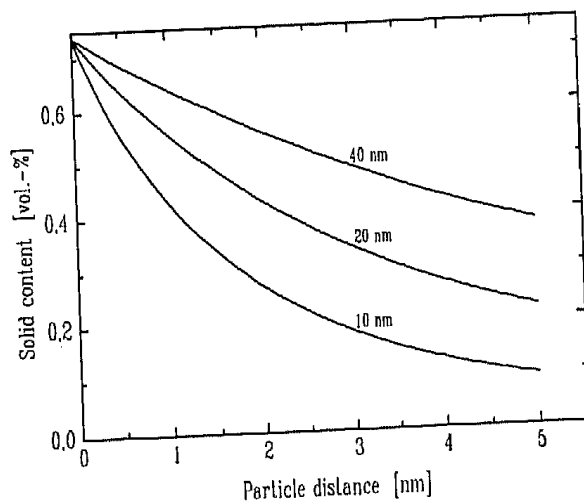


Fig. 1: Relationship between particle size, particle distance and solid content with spherical particles as model.

As one can clearly see, with very small particles only extremely low solid contents can be obtained. Since processing to ceramics with tolerable shrinkage rates requires green densities of more than 50 % by volume, the difficulties connected with the processing of small or nano-sized particles become obvious. On the other hand, small

particle systems are interesting for a variety of reasons. For example, they provide the potential of obtaining low sintering temperatures, especially if nano-sized systems are considered.

As already shown for metals, the diffusion coefficient in the surface layers of nano-sized metal particles is higher by some orders of magnitude compared to the solid materials [3]. In ceramic systems, however, there are no clear proofs for enhanced coefficients of diffusion, so far.

Investigations on monolithic sol-gel processing to ceramic parts have not been very successful up to now. Despite the fact that the particle size in the sol is in the nano range, strong particle-to-particle interaction leads to highly cross-linked gels ("green bodies") with very low solid contents (in the range of 10 % by volume) which only in a few cases (films, small PZT parts) lead to satisfying densification behavior [4]. The reduction of sintering tempe-

atures from gel monoliths clearly could be shown for supercritically dried alumina gels [4] or for small "monolithic" grains in the range below 1 mm by G. Messing [5]. A decrease of sintering temperatures can be expected from gel monoliths with uniform pore sizes. The fabrication of these monoliths, however, is extremely difficult due to stress formation during drying combined with a very low gel "green strength". Supercritical drying can overcome these problems, but results in extremely low green densities. The fabrication of ceramic parts through supercritical drying, therefore, only makes sense in a few exceptions. Despite this and based on the potential for low sintering temperature, it is interesting to process small particles in a way to obtain higher solid contents. For this reason, it seems to be necessary to modify the particle surface to reduce the particle-to-particle interaction. For this reason, the proposed techniques are wet processing or are casting techniques like tape and slip casting or electrophoretic shaping.

A serious problem is the availability of agglomerate-free submicron and nano-sized ceramic powders. Sol-gel methods seem to be an interesting way of synthesizing such particles because during the growth reaction, starting from molecular precursors, a nano-phase regime is obtained automatically. If it is possible to stop the growth reaction at this level, nano-sized ceramic systems should be accessible. As shown elsewhere, microemulsion techniques [6] or size-controlled growth processes [7] have an interesting potential for synthesizing nano-scale powders or slips as precursors for nano processing.

Another interesting topic related to the small particle size of colloids is the expectation to densify ceramic green bodies without grain growth. As described in [3] for metals, low-temperature densification is interpreted by high diffusion coefficients in the disordered areas of nano-sized grains, leading to almost no grain growth. Densification without grain growth leads to the possibility of obtaining a defect-free nano-crystalline dense structure and of tailoring the microstructure by a subsequent temperature treatment. This route would require a quasi-plastic deformation mechanisms to avoid transport mechanisms like surface or volume diffusion or liquid-phase sintering since these phenomena, in general, are related to grain growth.

Another interesting feature of colloidal processing is the possibility of attaching colloidal particles on the surface of micron or submicron particles. This leads to the possibility of „distributing“ low-concentration components very homogeneously within the green body or placing the desired components in the grain boundary, and several benefits can be expected from this type of process. Homogeneous distribution can lead to reduced stress formation during sintering, segregation processes during slip casting can be avoided, and in functional ceramics, additives can be positioned into the grain boundaries where they are very often desired, e.g. in varistor ceramics. To put additives on top of the surface of ceramic particles, several methods have been developed [8 - 9]. They are mainly based on electrostatical absorption of colloids charged in the opposite direction as the particle surface. For a general use of this route, surface modification techniques are required to tailor surface chemistry (including ξ -potential) in a desired way.

Whereas for micron and submicron powders electrical or electrosterical surface modification is an adequate means, for nano-sized particles other concepts have to be developed. The most important objective is to reduce the interparticular distance to obtain high package densities without causing agglomeration, as it is the case in surface charge stabilized systems. For this reason, the surface of the particles has to be modified by small molecules, showing a very high or selective interaction with the surface. The basic principles of this concept have been shown elsewhere [10]. This surface modification has to block the surface (for preventing particles from growing together), but has to be able to be removed during the sintering step without

causing secondary problems. This concept also has been used successfully to control the growth of particles in sol-gel techniques starting from molecular precursors [7].

Summarizing, one can say that the control of the interface between two different phases seems to be one of the substantial parameters in colloidal processing of ceramics. This is of interest for small particle synthesis by wet chemistry as well as for small particle processing to ceramic parts, even in combination with submicron and micrometer-sized ceramic powders. In the following, it will be demonstrated how this concept can be used for the synthesis of powders, for colloidal or nano processing as well as for a more conventional type of processing.

2. POWDER SYNTHESIS

There are different methods under investigation for the synthesis of nano-sized powders like vacuum condensation [3], chemical vapor condensation [1], chemical vapor reaction (CVR) [12] or laser pyrolysis [13]. These methods, in general, produce very fluffy nano-sized powders in crystalline form, but the production rates are still very low. CVR already has gained a pilot plant level in industry, and titanium nitride is one of the first available products.

Another possibility is wet chemistry, as demonstrated for zirconia [14], but in general, these powders are rather agglomerated. As already described elsewhere [6, 7, 10], microemulsion techniques can be used for the synthesis of nano-sized powders, too. Examples for successfully synthesized systems are ZrO_2 , Y_2O_3/ZrO_2 , $BaTiO_3$, PZT and others. The most important parameter of this special technology is the design of the interface between the two liquid phases in order to obtain a thermodynamically stable system ($\Delta G < 0$). In fig. 2 the basic principle of the microemulsion technique is shown. For optimizing the emulsion parameters, the HLB theory has been used [16]. This led to a three-component system, non-ionic emulsifier system very independent of the ionic strength of the salt solutions.

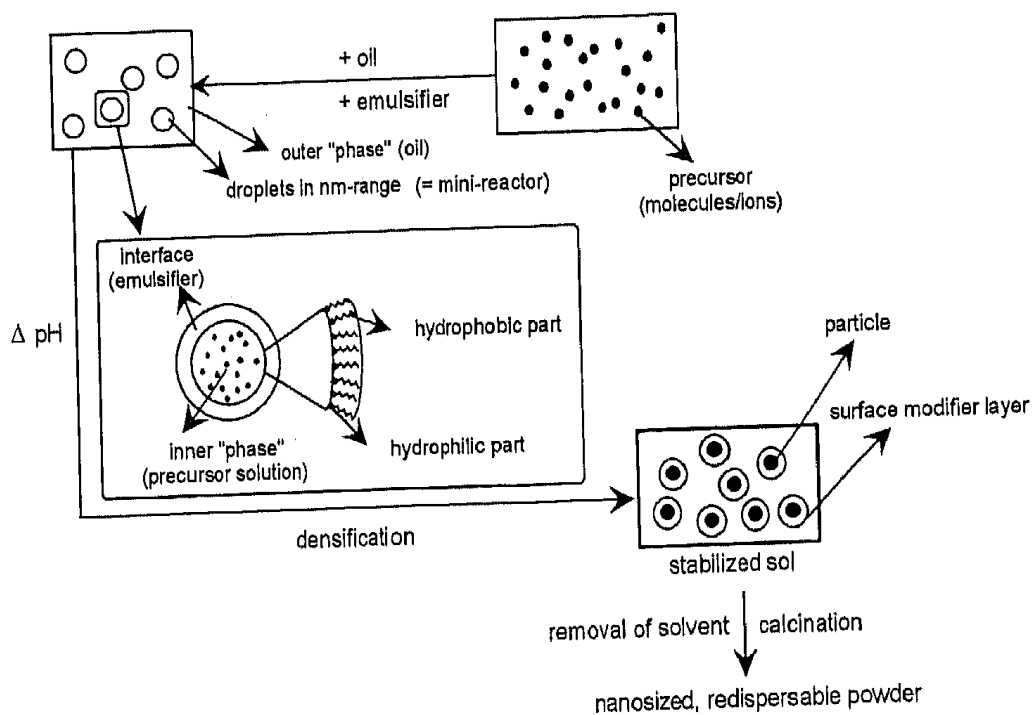


Fig. 2: Basic principle of microemulsion techniques for the synthesis of ceramic powders.

A major advantage of this synthesis process is the possibility of preparing multicomponent systems very easily since a wide variety of soluble ceramic precursors (e.g. salts) are available. Aqueous sols also can be used as precursors. Precipitation within the small water droplets can be carried out by pH change, using ion exchange processes or the addition of bases or acids. Additives, even in low concentrations, can be homogeneously introduced. Whereas for the formation of microemulsions the interface between the two liquid phases is dominating, after the precipitation the solid-to-liquid interface becomes important. It was found that the interfacial active components (emulsifiers) after precipitation act as protective coatings against agglomeration of the particles, leading to complete redispersibility. The calcination of the powders without agglomeration, however, is difficult, and very careful reaction conditions have to be established. However, as already shown for zirconia, a redispersable powder with a primary particle size of about 15 nm can be obtained.

From these results, the question arose whether a similar type of emulsifiers can be used as stabilizers during precipitation processes from homogeneous solutions, thus avoiding the emulsion step completely. As shown in [7], this can be achieved by changing the emulsifier composition. Adding an aqueous emulsion of the emulsifier mixture to an alcoholic solution of a zirconium alkoxide or a mixture of the alkoxide with an yttrium salt, nano-scale zirconia as well as yttria-stabilized zirconia powders can be prepared. The model developed for this process is shown in fig. 3.

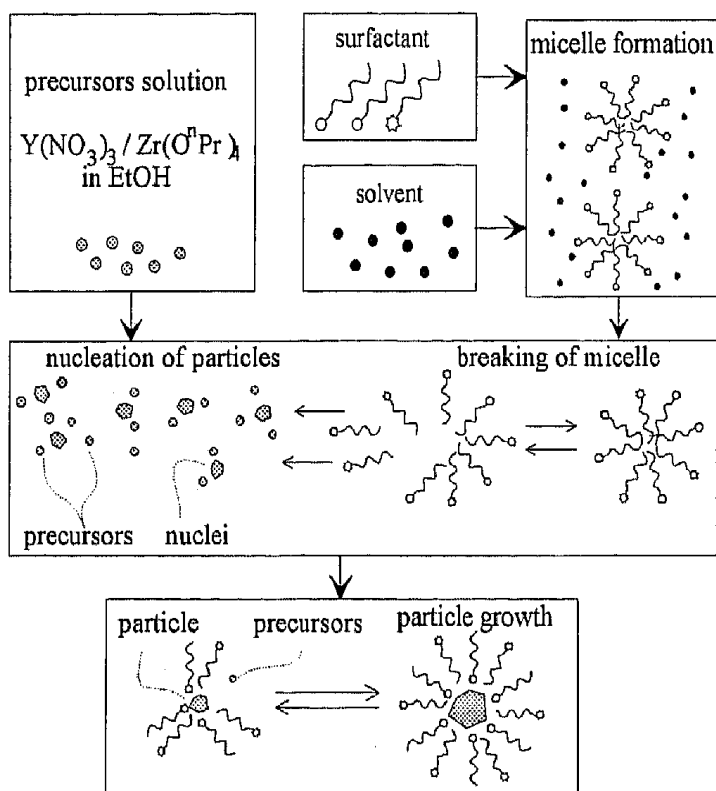


Fig. 3: Reaction model for the precipitation of agglomerate-free nano-sized ceramic powders in the presence of surface-active compounds.

The model suggests that the original emulsion formed by the surface-active compound, which has a micelle type structure, gets reorganized in presence of the precipitating zirconia system. Through this reorganization process, the growing system is protected by the tenside molecules, preventing the growing particles from agglomeration. In fig. 4, a TEM micrograph of the fast derived nano-scale powders is shown. A

comparison of the two routes shows that the surface-controlled precipitation process leads to substantially higher yields per liter (20 g of dried powder compared to 100 g). First sintering experiments using these powders show a substantial reduction of sintering temperatures below 1200 °C.

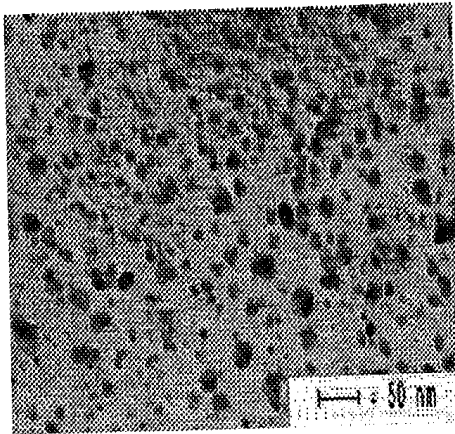


Fig. 4: SEM micrograph of Y_2O_3/ZrO_2 with a particle size less than 15 nm.

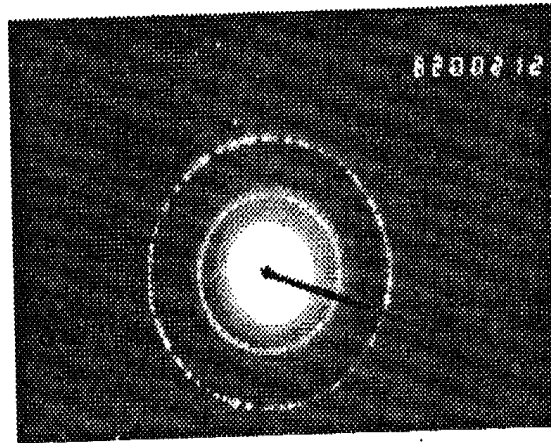


Fig. 5: Electron diffraction pattern of nano-crystalline ZrO_2 particles of ZrO_2 /methacrylate nanocomposites [17].

Other surface modifiers, such as methacrylic acid, have been used for the fabrication of zirconia nano-particle-containing composites. It could be shown that within an inorganic-organic composite matrix, even at temperatures below 120 °C, nano-crystalline zirconia particles with a size between 2 and 4 nm can be grown [17]. In fig. 5, the electron diffraction pattern is shown, indicating clearly a reflection to be attributed to crystalline phases. The analysis shows that the majority of these phases can be identified as monoclinic zirconia. Due to the particle size, which is in the range of 2 nm, these composites are highly transparent and processed to optical materials for wave guides and microlens systems [18].

These results show that there is an interesting potential in synthesizing nano-crystalline ceramic materials by surface tailoring. The future objectives are to investigate how far these nanopowders can be used for low-temperature sintering of oxide ceramics.

3. SURFACE TAILORING FOR PROCESSING OF NANO-SCALE SYSTEMS

The basic principle of surface modification for the synthesis of nano-scale particles has already been discussed in chapter 1. The question arises whether this principle can be generalized and used for the development of processing techniques, too. First investigations have been carried out with boehmite as a model system [19, 20]. For this reason, stronger agglomerated commercially available boehmite has been surface-treated with propionic acids and deagglomerated down to particle sizes between 15 and 40 nm. After extensive washing, these systems still show a remarkable content of carboxylic groups, but no free acids as proved by DRIFT spectroscopy: Diffuse Reflectance Infrared Fourier Transform spectroscopy. In fig. 6, the infrared spectra of the free carboxylic acid and the surface compound are compared. It has to be concluded that a surface compound has been formed with bonds very similar to those observed in salts of aluminum with carboxylic acids.

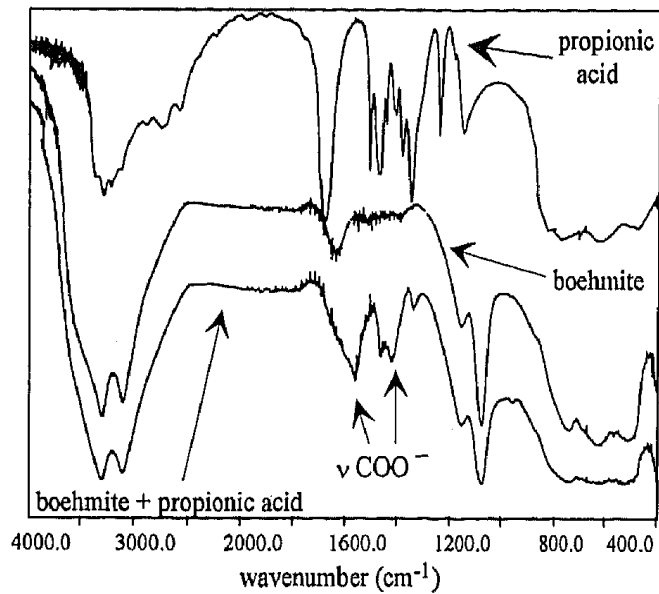


Fig. 6: IR spectra of free carboxylic acid, as received boehmite powder and the boehmite/propionic acid surface compound.

From the surface-modified boehmite sols high solid content can be prepared without gelation, which are highly translucent. Slips can be concentrated up to solid contents of 40 - 45 vol.-%, which then exhibit rheological properties suitable for extrusion processes. In fig. 7, the a piece of a green foil prepared by rolling is shown.



Fig. 7: Translucent green body of modified boehmite.

For improvement of the extrusion properties some weight percent of organic additives (cellulose derivatives) are added. The total amount of organics does not exceed 6 wt.-% (3 wt.-% is attributed to the surface-modifying propionic acid). After freeze drying of the extruded specimens, the green density is in the range of about 60 % by

volume, enabling the system to be fired to porous alumina at 1250 °C. Of course, boehmite is not a very good raw material for producing dense α -alumina, but it has been used as a model due to its commercial availability and the fact that it can be deagglomerated to nano-scale particles rather easily. There is a good probability to obtain similar results with nano-scale α -alumina as soon as it is available in sufficient amounts.

In the case of titanium nitride it was possible to obtain 40 nm titanium nitride produced by the chemical vapor reaction process (CVR) from H. C. Starck company. The as received powder is strongly agglomerated, and systematic investigations with several surface modifiers have been carried out to deagglomerate these systems. In fig. 8, the results of the deagglomeration experiments are shown.

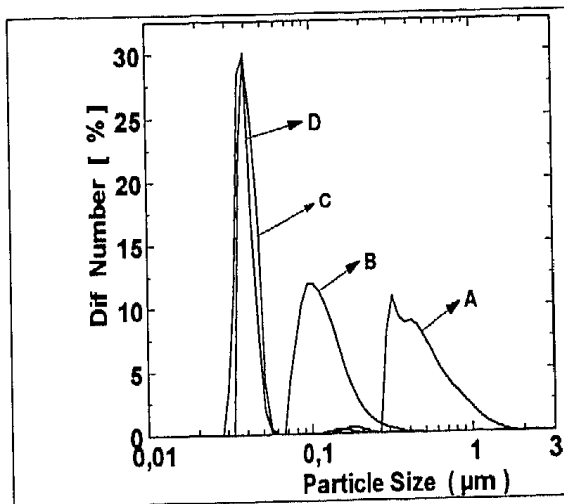


Fig. 8: Results of dispersion experiments with agglomerated 40 nm TiN using different surface modifiers. A: ammonia, B: amino propionic acid, C: guanidine propionic acid, D: guanidine carbonate.

As fig. 8 displays, the guanidine derivatives gave the best results. The powder could be redispersed to its primary particle size with a very narrow distribution. The ESCA spectra of the titanium nitride powder show that the particles are covered with a thin oxide layer. The effect of the guanidine derivatives have, therefore, been explained by the formation of a surface chelate complex and a subsequent electrosteric mechanism for preventing reagglomeration [21]. Green bodies with densities exceeding 50 % of theory could be obtained by simple colloidal filtration which could be densified pressureless at temperatures below 1300 °C to high densities (> 98 %) without significant grain growth. In fig. 9, densification and grain growth vs. temperature are shown. Almost full densification is obtained before grain growth starts.

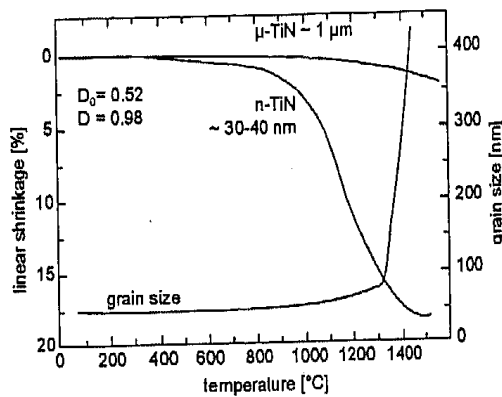


Fig. 9: Densification and grain growth of nano-scale titanium nitride green bodies prepared from a surface-modified (guanidine propionic acid) powder (40 nm).

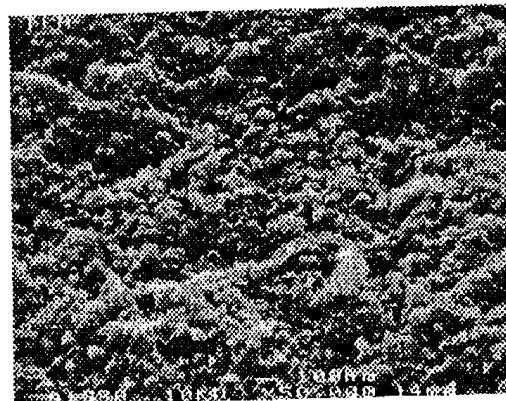


Fig. 10: Microstructure of TiN specimens sintered at 1300 °C.

Above 1300 °C, crystal growth starts. Fig. 10 shows the microstructure of the sintered titanium nitride.

These results demonstrate that it is possible to employ “conventional” ceramic processing techniques with nano powders. Furthermore, it could be shown that densification can be separated from grain growth (microstructure formation) almost completely. This opens new possibilities for ceramic processing including new routes for microstructure tailoring. Further investigations will be directed to properties of sintered parts obtained by this process and to determine the deformation or transport mechanisms responsible for densification.

Using these techniques, coatings on metals or ceramics can be carried out by a simple dip coating process followed by a sintering step between 1150 and 1250 °C. Fig. 11 compares the

microstructure of TiN coatings prepared by CVD and the dip coating process after sintering, respectively.

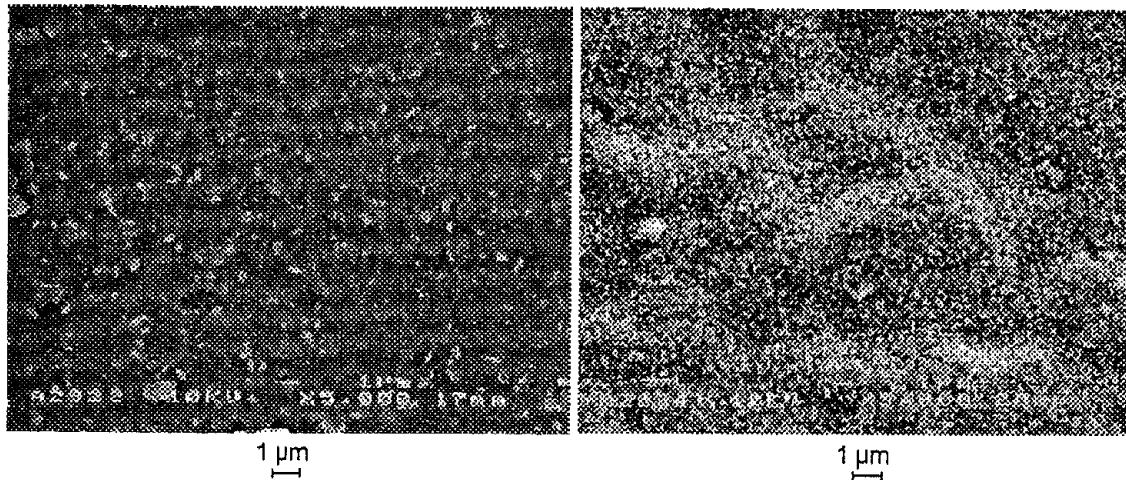


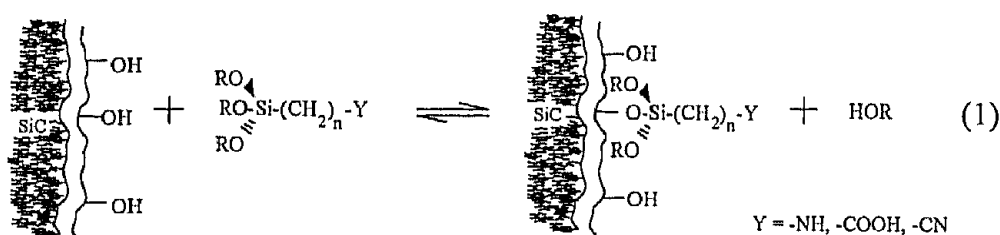
Fig. 11: SEM micrographs of the microstructure of titanium nitride coatings on an alumina substrate prepared by CVD (a) and dip coating followed by sintering (b).

As one clearly can see, the sol-gel coating is very smooth, with grain sizes in the region of the starting powder.

4. USE OF SURFACE MODIFICATION FOR SLIP CASTING AND ELECTROPHORETIC PROCESSING

In the previous chapters, it was shown that surface and colloidal chemistry can be used for the synthesis of small particle as well as for nano-processing. This chapter will focus on the question how far these techniques can be used for improving the conventional type of processing, especially if sintering additives are required in a very finely dispersed form, as it is the case for silicon carbide.

Pressureless sintering of silicon carbide generally requires nano-scale carbon black for the reduction of the SiO_2 covering the SiC powder [22]. However, processing of SiC slips containing nano-scale carbon black by casting techniques like slip or pressure casting is rather difficult. Segregation processes with the effect of additive separation takes place during the casting procedure since carbon black with particle diameters below 20 nm, is able to pass through the pores of the built-up ceramic body as well as of the mould. The segregation leads to strong fluctuations of the carbon black concentration within the green specimens which finally result in high residual stresses and cracks in sintered parts. As shown in [23], this problem can be overcome if the carbon black is directly coupled to the top of the silicon carbide particles. For this reason, the silicon carbide surface (SiO_2 layer) has been modified by different silanes which are chemically bond to the surface (eq. 1).



Using this approach, the surface of the silicon carbide can be modified in a wide range just by proper choice of the suitable silane functions [24]. Thus, acidic and basic surfaces have been obtained, and the zeta-potential of the silicon carbide can be varied in a wide range as shown in fig. 12.

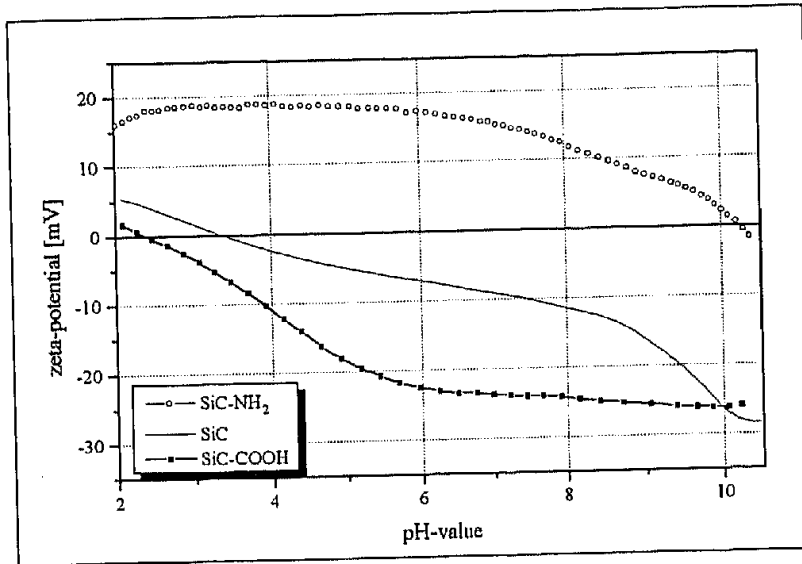


Fig. 12: pH dependence of the zeta-potential of unmodified and modified silicon carbide.

This leads to another interesting topic, the adaption of the zeta-potential of different ceramic powders, especially if stable slips have to be prepared from powders with very different surface properties.

For bonding carbon black to SiC surfaces, amino group-containing silanes have been used for surface modification. Acidic carbon black was precipitated on the top of the silicon carbide grains, as shown in fig. 13.

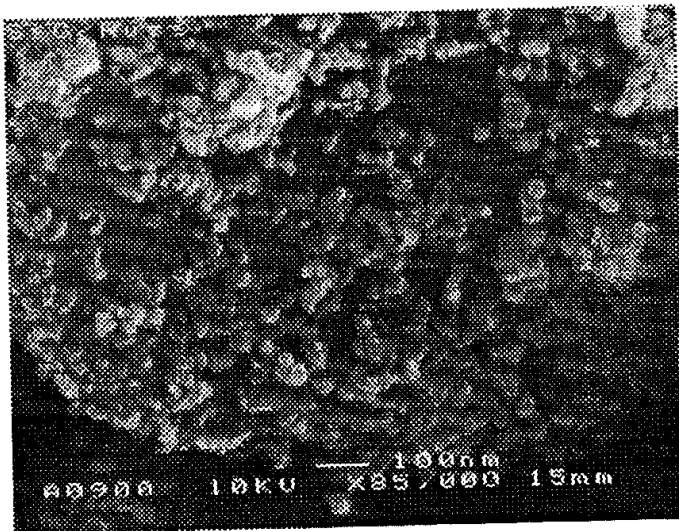


Fig. 13: Surface of silicon carbide modified by carbon black. The small particles represent the carbon black.

The amount of surface precipitated carbon black necessary for the reduction of the SiO₂ layer can be adjusted very precisely so that a complete reduction of SiO₂ is achieved

In lab experiments, crucibles have been produced by pressure slip casting, comparing the conventional (non-precipitated) method and the new approach. The crucibles have been sintered pressureless at 2080 °C to full density, and the results are shown in fig. 14.

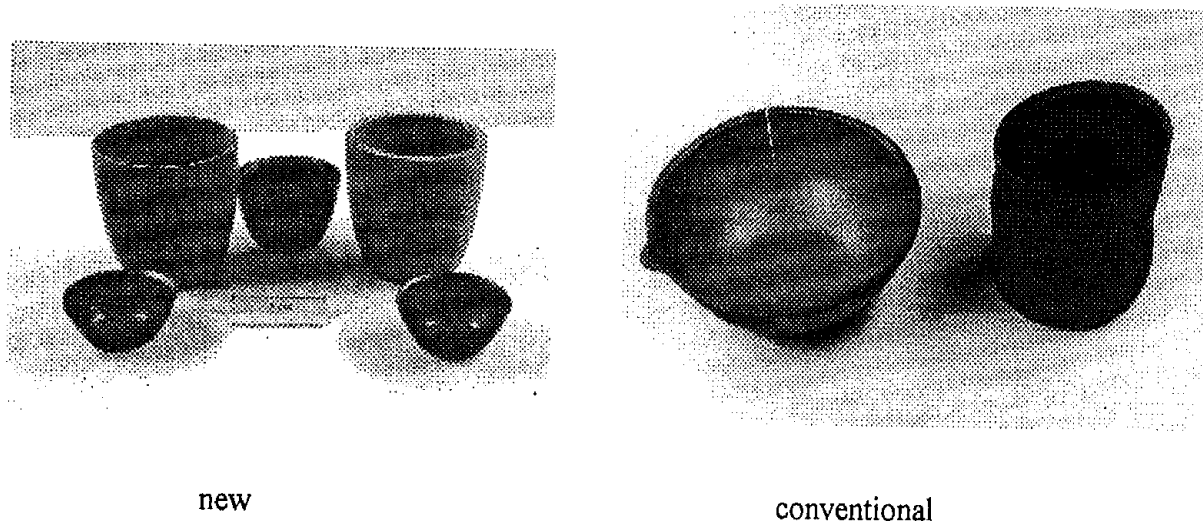


Fig. 14: SiC crucibles prepared by pressure casting with immobilized (left side) and without immobilized (right side) carbon black and pressureless sintered at 2080 °C; B₄C as sintering aid.

As one can see, parts prepared from the unmodified system formed cracks during sintering which was attributed to the strains built up during densification due to the inhomogeneous distribution of carbon black. In the modified case, no change of the shape can be detected, and the sintering process leads to very regular shaped crucibles. In fig. 15 the microstructure of such sintered parts is shown consisting of very regular grains.

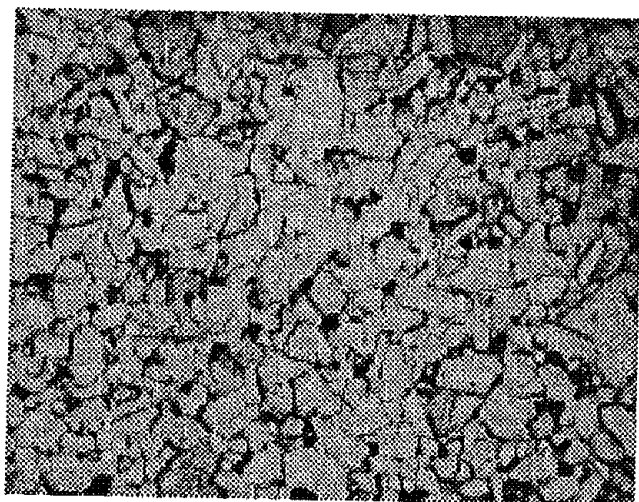


Fig. 15: SEM micrograph of pressureless sintered SiC using carbon black-modified SiC powder and B₄C as sintering aid.

The mechanical data of the system are: bending strength: 600 - 800 MPa, K_{1C}: 2,9 MPa · √ m, hardness (HV_{0.5}): 31 GPa. The fracture toughness is still rather low, but can be improved by well-known mechanisms. Anyway, the data are promising for pressureless sintered SiC ceramic conventional temperatures.

The tailoring of the surface properties including the precipitation of nano-scale particles leads to interesting processing possibilities such as making particulate systems compatible to each other (e.g. SiC and Al₂O₃) for stable slips, preparation of shell type particulate multicomponent systems or preparation of particulate systems with dopants attached to the particle surface to position them homogeneously into the grain boundaries.

Whereas with slip casting of SiC, it is sufficient to precipitate nano-scale additives on top of the surface of the major component, in the case of electrophoretic shaping which is an interesting alternative for a variety of technologies, e.g. for coatings, the requirements are different. Generally, it is necessary that all components are transported to the electrodes with the same velocity, to avoid separation effects. For this reason, surface modification methods have

to be employed suitable for a variety of different surfaces, depending on the type of components.

Surface analysis by DRIFT spectroscopy showed that SiC and B₄C are covered with ≡SiOH and =BOH groups [25], respectively, which are weak acids. For this reason, polyethylene imine (PEI) was investigated as a surface modifier to use the acid/base interaction as the coupling principle for B₄C and SiC as well as for acidic carbon black. Moreover, the adsorption mechanism of a polymeric type of base should lead to a stable adsorbed phase. The question arises whether the surface charges can be tailored for the three components in a way that equal transportation rates in the electric field are obtained. In fig. 16 the surface charge as a function of (PEI) load and a model for the surface modification are shown.

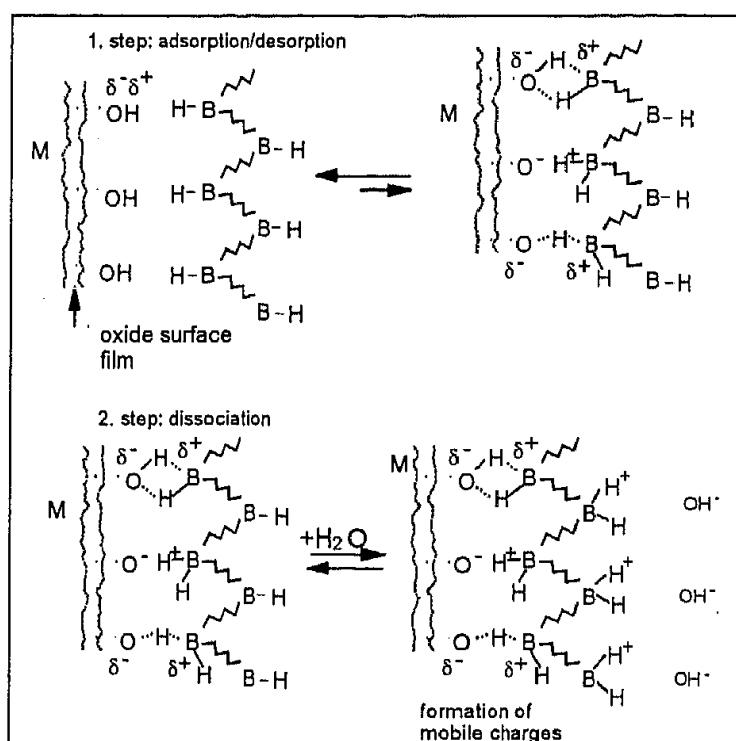
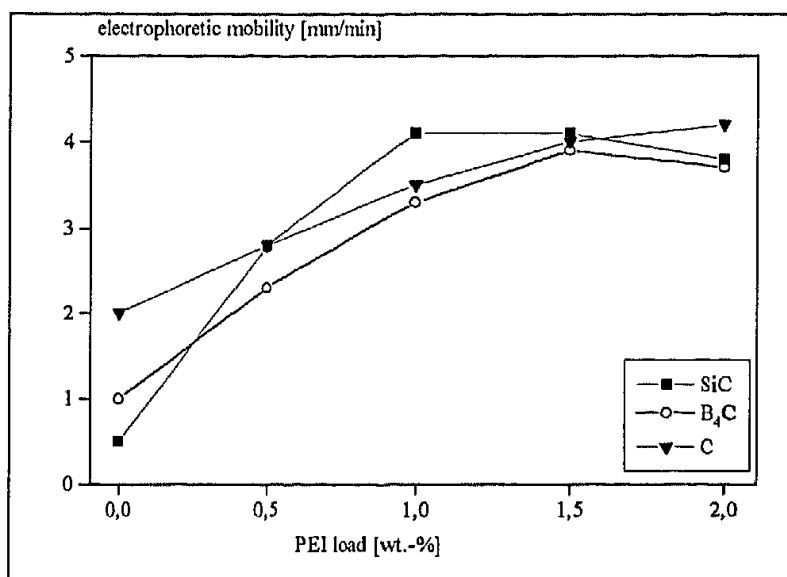


Fig. 16: Iso charge regime as a function of the PEI load (a) and an adsorption model of PEI to the surfaces of SiC, B₄C and carbon black (b).

As one can see, an "iso charge" regime exists for all three components (charge/surface unit). Electrophoretic deposition experiments have been carried out in alcohol as solvent, the experimental detail of which are given elsewhere [23]. Analysis of the component distribution (depth profiling) in a ceramic body of 5 mm in thickness has been carried out. The results show that within the exactness of the method (chemical analysis of thin layers) no change of composition can be detected.

The bodies have been pressureless sintered to full density at 2070 °C and show a very homogeneous microstructure with an average grain size of about 5 µm.

5. CONCLUSION

The application of surface and colloidal chemistry is a suitable means for tailored ceramic processing, starting from the synthesis of nano-scale powders, processing them to high density green bodies as well as for improving conventional type of wet processing like slip casting or electrophoretic deposition. This opens interesting new routes such as low sintering nanoceramic route by separating densification from grain growth, superplastic deformation or sub-µm high pressure slip casting techniques.

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