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PROCESSING AND SINTERING OF NANOSIZED TiN

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The concept of surface modification of nano scale particles with short chained organic molecules has been used for the preparation of deagglomerated slurries of n-TiN. Using guanidine propionic acid as surface modifier, the strongly agglomerated powder could be redispersed to its primary particle size of 30 to 40 nm. From such suspensions green specimens with densities of 50 % could be prepared by pressure filtration, which could be sintered to high densities (> 96 %) at temperatures below 1400 °C without significant grain growth.

1. INTRODUCTION

One important prerequirement for the utilization of nanosized ceramic powders as starting material for advanced ceramic materials is the development of processing and forming techniques which allow the production of defect-free green parts with high densities and homogeneous pore size distributions. The use of nanoparticles is interesting for densifying ceramic parts at temperatures where no rapid grain growth takes place. This should be expected from the large excess energy of the disordered phase near the particle surface[1], leading to enhanced diffusion coefficients. In order to achieve these goals, two main problems have to be overcome: agglomeration of particles and package density in green parts. Agglomeration generally occurs in particulate systems and results from attractive interparticle forces like van-der-Waals forces. In order to control the state of agglomeration, powder processing is carried out in dispersions creating repulsive interparticle forces which keep the particles apart from each other. Repulsive forces are obtained by the interaction of the particle surface with a certain surfactant, and in most cases lead to an electrostatic or electrosteric stabilization mechanism. The major draw-back of both stabilization mechanisms in connection with nano-scale particles are nm-ranging repulsive forces, leading to low maximum solid contents of the dispersion as well as of the green parts[2].

In order to overcome these problems, the concept of surface modification of nano-scale particles with short-chained organic or organometallic molecules providing short-

range steric repulsive forces, has been developed As shown in [3] for an agglomerated boehmite powder with a primary particle size of about 15 nm, surface modification with short-chained carboxylic acids leads to completely deagglomerated slurries, which could be concentrated to extrusion pastes with high solid contents (< 50 vol.-%) Extrusion yielded green parts with green densities up to 60 % of theory after drying This concept has been applied to a nano-scale TiN powder in order to develop a processing technique which will lead to high density green parts and which can further be used for the evaluation of the potential of a nano-scale ceramic green microstructure in sintering process

2 EXPERIMENTAL

The starting powder was characterized with XPS-spectroscopy, X-ray diffraction and TEM. For slip preparation 45 g of nano-scale TiN-powder (H. C. Starck, FRG) were dispersed in 55 g of a water/ethanol mixture under stirring. To this suspension 0.1 to 5 wt % tetramethylammoniumhydroxid and guanidine propionic acid with regard to the solid content were added, ultrasonically agitated, sieved and used for further experiments. The particle size of the dispersed TiN has been measured by photon correlation spectroscopy, dynamic laser scattering and by TEM. Following the above procedure aqous slips of up to 40 wt % solid content were prepared From these slips disc-shaped green bodies (diameter 50 mm, thickness 3 mm) have been produced by pressure filtration. The obtained green bodies were first dried for 24 h in a water saturated atmosphere using a desiccator. The drying procedure was completed by drying the green bodies in an oven at 70 °C under flowing nitrogen

3 RESULTS AND DISCUSSION

3.1 Powder Characterization

The starting TiN powder was characterized with respect to particle size and morphology, crystallinity and surface properties In fig. 1 a TEM micrograph of the as received powder is shown. Fig 1 demonstrates that the powder consists of primary particles with diameters between 20 and 40 nm and a more or less spherical morphology As expected, the particles form agglomerates of irregular shape and size Electron beam diffraction as well as X-ray diffraction (fig 2) reveal a nanocrystalline structure of the particles In both cases the observed pattern could be attributed to osbornite the crystalline modification of TiN
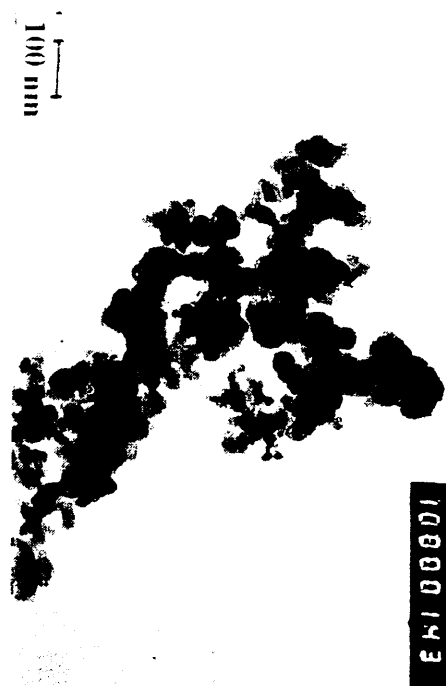

FIGURE 1. TEM picture of the as-received TiN powder.
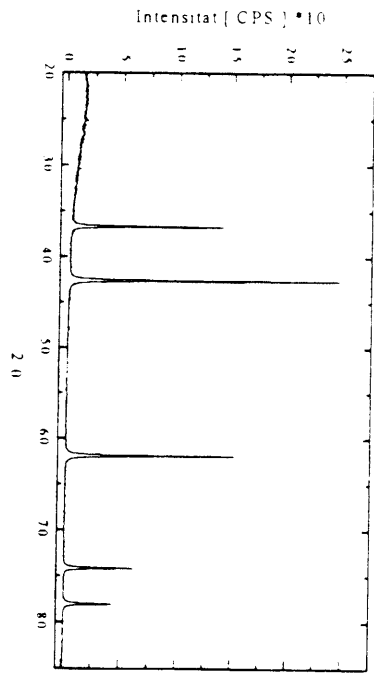
100 nm

Intensität [CPS] *10

2 θ

FIGURE 2. X-ray diagram of nano-scale TiN.

Due to the small particle size, line broadening occurs in the X-ray diagram from which the crystallite size was calculated to 20 nm This is in good agreement with the TEM results and indicates that the particles consist of nanometer-sized single crystals.

According to the concept of surface modification of nano-scale particles the knowledge of the surface chemical properties of the starting powder is an additional prerequirement since these properties will determine the selection of suitable surface modifiers For this reason the powder surface was investigated by XPS spectroscopy In fig 3 the XPS spectrum of the as received TiN powder is compared with the XPS spectrum of commercially available TiO_2
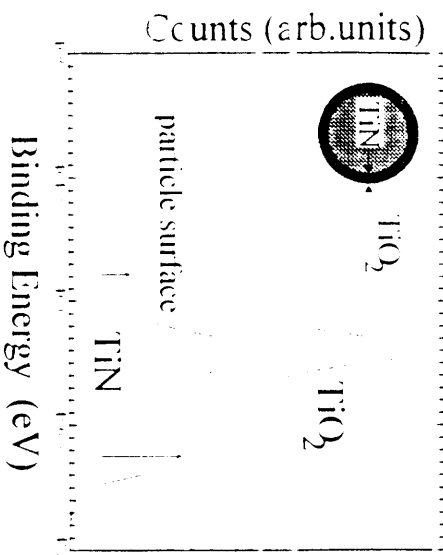
FIGURE 3 XPS spectra of nano-scale TiN (a) and TiO$_2$ (b).

In the XPS spectrum of the TiN four lines are observed which can be attributed to two different chemical species. The lines around 463 eV and 455 eV result from TiN whereas the strong line around 458 and the broad line around 464 eV must be attributed to TiO$_2$. From the XPS measurements, it therefore can be concluded that the TiN particles are covered by a TiO$_2$ layer which will determine the surface properties.

Further information about the surface properties were obtained from pH measurements. Following the procedure described in DIN ISO 787/IX, a pH value of 5.8 was determined.

This result shows that the TiN powder exhibits weak acidic surface properties similar to pure TiO$_2$. These properties are associated with the TiO$_2$ layers of TiN particles and must be attributed to acidic Ti-OH surface groups which undergo dissociation when the powder is dispersed in water. For the preparation of completely deagglomerated suspensions of n-TiN by a surface modification technique as described in [4] the pH measurements also indicate that a sufficiently strong acid/base interaction between the particle surface and a modifier will only take place with strong bases. For this reason, different strong organic bases like tetraalkylammonium hydroxides and guanidine derivates have been tested as dispersing agents. The preparation of suspensions was carried out in a water/ethanol mixture (50/50) and the particle size distribution was determined by photon correlation spectroscopy (fig 4)
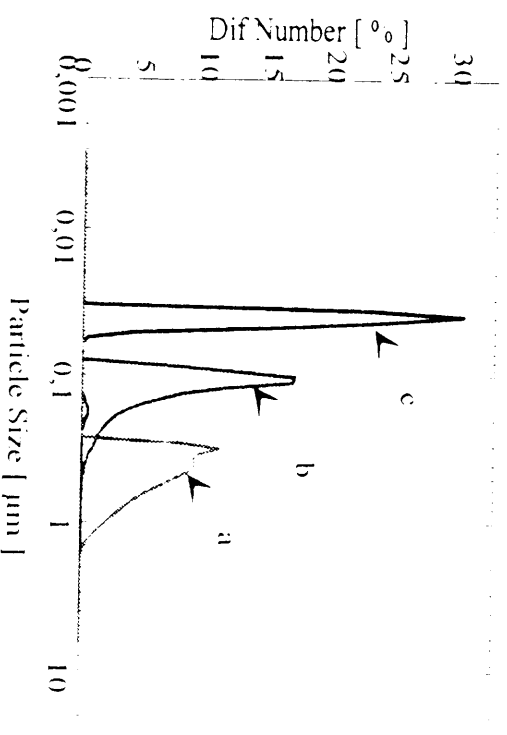

FIGURE 4. Particle size distributions of ethanolic n-TiN slurries using different dispersing agents.
a as received powder without dispersing agent.
b n-TiN + C$_4$H$_{11}$NO (Tetramethylammoniumhydroxid, TMAH)
c n-TiN + (C$_4$H$_9$)$_3$NOH (Guanidin propionic acid, GPA)

From the particle size distribution in fig 4a it can be seen that the n-TiN forms agglomerates in the range of several hundred nanometers without any dispersing agent. In contrast, the addition of TMAH leads to a reasonable decrease of particle size (80 - 400 nm), but the primary particle size of 30 - 40 nm is not reached in water. If guanidine propionic acid (GPA) is used as a dispersing agent a narrow particle size distribution between 30 and 60 nm is obtained which is in excellent agreement with the primary particle size of the powder as determined by TEM. In order to explain the different dispersion forces of TMAH and GPA, respectively, the model shown in fig 5 was developed.

Both compounds can undergo an acid/base reaction with the particle surface, but will result in two different stabilization mechanisms. TMAH can only abstract protons from Ti-OH groups, which will lead to a negatively charged particles' surface and an electrostatic stabilization mechanism. A slightly different situation is found for GPA. Beside the ability to abstract protons, GPA can also coordinate other Ti-OH groups on the particle surface
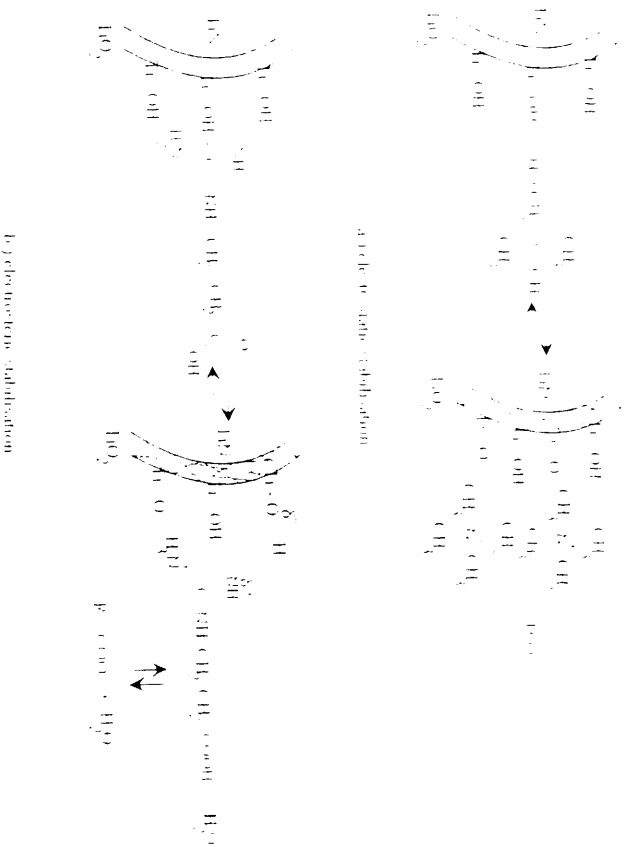
FIGURE 5   Model for the deagglomeration of n-TiN by IMAH (a) and GPA (b), respectively, in aqueous solution

Both reactions will act GPA to the particle surface forming a chemically stable chelat-like ring system. In an additional step dissoziation of the carboxyl group can take place and negatively charged particle are obtained. But due to the surface modification the suspension is stabilized by an electrosteric stabilisation mechanism. The nano dispersed suspension was shaped by a pressure filtration process into disc shaped green bodies. Green bodies with densities between 48 and 52 % of the theory were obtained These specimens were used in sintering experiments, and in fig 6, the dilatometer curve of a n-TiN is compared with the sintering curve of a sub-μm TiN

As can be seen from fig 6, sintering of n-TiN starts between 800 and 1000 °C and is finished around 1400 °C with a total linear shrinkage of 18 %. At this temperature a final density above 98 % is achieved In contrast, the specimen prepared from a coarser TiN powder (0.5 - 1 μm) exhibits a much lower sintering activity, and no densification is observed up to 1600 °C. In fig 7, a comparison of the green as well as sintered micro structure prepared from n-TiN is given
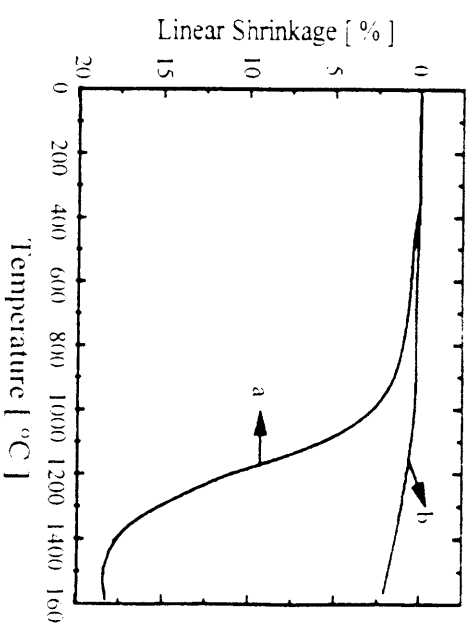
FIGURE 6: Dilatometer curves of TiN specimens prepared from a nano-scale TiN powder (a) and a conventional sub-μm powder (b)
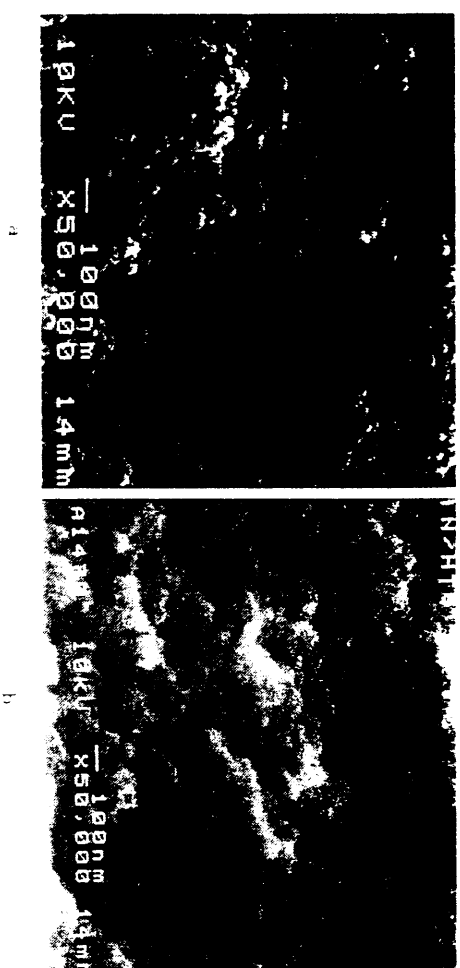
FIGURE 7: Microstructures of green specimens (a) and sintered parts (b) prepared from n-TiN

The green samples show a homogeneous microstructure with a good arrangement of nano-scale particles of particle sized in the range of 30 - 40 nm Fig 7b shows the microstructure of a sample sintered at 1300 °C for 2 min in flowing nitrogen atmosphere The relative density of the sintered sample was 0.96 The observation of the fracture surface indicates the average grain size to be 70 nm It is evident that no

significant grain growth takes places after this sintering threatment. From this obser-vation, it can be concluded that nano-scale particles offer the unique opportunity of separating densification and grain growth during sintering, which gives rise for tailored microstructures as well as properties by post-thermal heat treatment.

Determination of the hardness of sintered specimens with a density of about 98 % gave a $HV_{0.1}$ value of 21.5 GPa. Taking into account that conventional TiN exhibits a hardness of $HV_{0.1} = 20.6$ GPa if the density exceeds 99 % of the theory, the hardness of the less dense nano structured ceramic is quite high.

4 CONCLUSION

It could be proved that surface modification of n-TiN with short-chained organic molecules provide a suitable route for the preparation of deagglomerated suspensions of nano-scale particles and that such suspensions can be processed to green speci-mens with high densities and a homogeneous microstructure. Sintering experiments reveal that the specimens densify without significant grain growth, which opens new opportunities for microstructure tailoring by post-heat treatment. An interesting result is the fact that during densification almost no significant grain growth takes place, although effective mechanisms are responsible for the mass flow. The nature of these mechanisms is not yet known but should result from the structure of the nano particles and is an objective of further investigations. The „separation" of the densification regime from the grain growth regime opens interesting possibilities for microstructure tailoring

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CONTROL AND CHARACTERISATION OF MICROSTRUCTURE IN SOL-GEL FILMS FOR OPTICAL DEVICE APPLICATIONS

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Sol-Gel is a promising technique for fabrication of silica-based layers for integrated optics, particularly silica-on-silicon. The materials fabricated in this way are typically microporous, and these micropores are of considerable interest, both because of their relationship to the strength and shrinkage of the films, and because they provide possible locations for the insertion of dopants. This paper will describe techniques by which pore structure can be characterised in films, particularly ellipsometry (including molecular probe ellipsometry) and infra-red spectroscopy. Results are presented which show the influence of fabrication technique and process variables, particularly heat treatment, on this structure.

1. INTRODUCTION

One of the main benefits sol-gel processing offers for applications in integrated optics is its great flexibility, in terms of the wide range of structures and compositions that can be produced. On the other hand, there is a major disadvantage in that the large degree of shrinkage inherent in the process causes stress levels which make the film thicknesses required for integrated optics (>10 μm) very difficult to achieve. The atomic scale structure plays a crucial role in both these aspects, and therefore it is important to be able to characterise and control this structure. It is the capillary forces associated with solvent evaporation from micropores which are primarily responsible for stress and shrinkage. However, these micropores can also provide sites for insertion of dopant species to

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