

COLLOIDAL PROCESSING AND SINTERING OF NANO-SCALE TiN

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ABSTRACT

Surface modification of nano-scale TiN powder with guanidine propionic acid was used for the preparation of well dispersed slurries. The starting powder could be completely deagglomerated for modifier concentrations exceeding 7.5 wt.-% at pH = 9. Such slurries (≤ 40 wt.-% solid content) behave like an ideal Newtonian liquid. Green compacts with relative densities around 50 % were prepared by pressure filtration. The specimens are characterized by a homogeneous green microstructure with pore sizes in the range of 3 to 10 nm, which could be sintered to high density (> 96 %) below 1400 °C. Up to densities of 96 % grain coarsening can be neglected, but further densification was accompanied by an exaggregated grain growth.

INTRODUCTION

One of the most interesting features of nano-scale ceramic powders is their high intrinsic sintering activity which results from the large excess of surface free energy [1, 2]. From this point of view densification of nano structured ceramic green parts should take place at rather low temperatures. An essential prerequisite for the utilization of this potential for ceramic technology is the availability of processing techniques which lead to green compacts with high density and homogeneous pore size distribution. Recently, it was shown that the desired properties can be realized if powder processing is carried out in suspensions using the concept of surface modification of nano-sized particles with short chained organic or organometallic molecules providing short range steric repulsive forces [3, 4, 5]. Using this technique, nano-scaled TiN could be processed to green compacts with relative densities above 50 % and could be further sintered to high densities (> 96 %) below 1400 °C, maintaining a nano-scaled microstructure [6]. However, for further evaluation of this technique, more detailed information about the whole process are needed, especially about the properties of the suspensions, because they will strongly influence the characteristics of green compacts as well as the densification behavior. In this paper the properties of nano-scale suspensions are reported as well as some new results about densification of n-TiN.

EXPERIMENTAL

The starting powder was nano-scale TiN with a specific surface area of 56 m²/g and a primary particle size between 30 and 40 nm (H. C. Starck, Laufenburg, FRG). Surface modification with guanidine propionic acid (GPA) as well as the preparation of slurries (40 wt.-%) was carried out

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according to [6]. For systematic investigations of suspension properties the amount of GPA was varied between 0.5 and 20 wt.-% in the pH range of 5 to 10 using solid contents between 10 and 50 wt.-%. Deagglomerations was supported by ultrasonic agitation. Disc-shaped green bodies (diameter 50 mm, thickness 3mm) were prepared by pressure filtration. Drying of wet compacts was performed in a controlled atmosphere of 80 % relative humidity at room temperature. Sintering was carried out between 1200 and 1400 °C in flowing nitrogen. Suspensions were characterized with respect to viscosity, zeta potential, particle size and particle size distribution using standard techniques. The pore size distribution of green parts was determined from nitrogen adsorption/desorption isotherms using the BET theory. Density was measured by Archimedes principles. Microstructure was characterized by observing of the fracture surface of green bodies as well as sintered parts in a high resolution SEM (JEOL, JSM 640). Due to the intergranular fracture mode the average grain size of sintered samples could be determined from the SEM pictures of fracture surface using the linear intercept method.

RESULTS AND DISCUSSION

Following the procedure described in [6], the as received TiN powder was dispersed in an ethanol/water mixture by using of 5 wt.-% GPA as modifying agent. Since GPA has a betaine structure, the colloidal properties of suspensions should be governed by the dissociation of the carboxyl groups which can be influenced by pH if the GPA is adsorbed through the amino groups according to the model in Fig. 1.

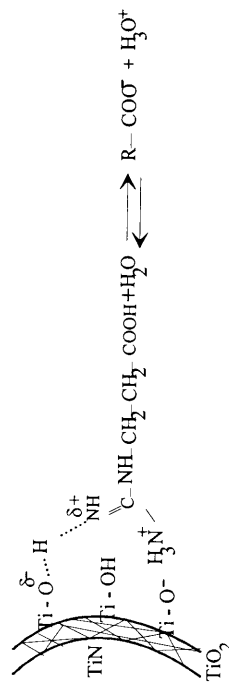


Fig. 1: Interaction of GPA with the TiN surface [6].

The pH dependent zeta potential of modified powder is shown in Fig.2. For comparison, zeta potential of the same powder without surface modification is also given. The zeta potential vs. pH curve of modified powder clearly supports the binding model presented in Fig. 1. Due to the surface modification, the isoelectric point of the as received powder is shifted from pH = 4,8 to pH = 3,2. At the same time, higher negative zeta potentials are observed for pH values greater than 4. From these results stable suspensions are expected for pH values above 4. Systematic investigations revealed that suspensions stable for several months are obtained at pH 8 - 9. However, the powder could not be completely deagglomerated with 5 wt.-% GPA at pH 9 as indicated by particle size measurements. This was attributed to an insufficient coverage of the TiN particles with GPA. In order to determine the optimum concentration the amount of GPA was varied between 0.5 and 20 wt.-%, and particle size distribution was measured by photon correlation spectroscopy. Fig. 3 shows the measured TiN particle size at pH = 9 as a function of the GPA concentration.

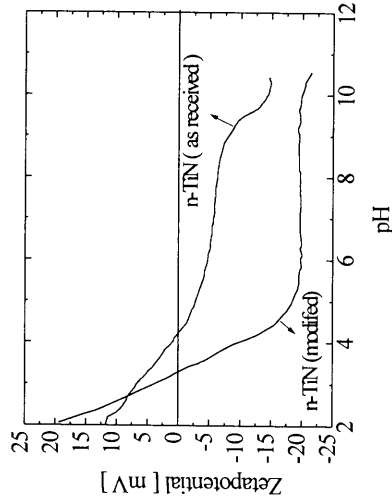


Fig. 2: Zeta potential vs. pH of n-TiN powder before and after surface modification with 5 wt.-% guanidine propionic acid

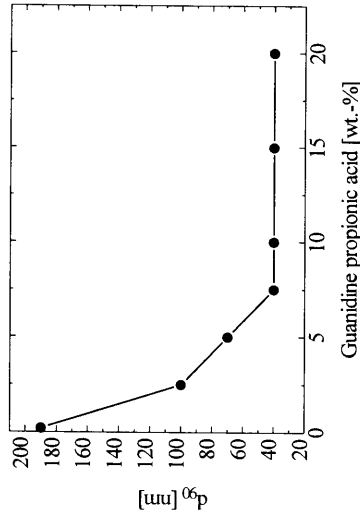


Fig. 3: Influence of GPA concentration on the particle size of the suspension at pH = 9.

Up to GPA concentration of 7.5 wt.-% a continuous decrease of particle size was observed. Higher GPA concentrations showed no effect on particle size. This results indicated the optimum GPA concentration to be 7.5 wt.-%. Therefore, slips for further experiments were prepared from powder which was surface modified by using of 7.5 wt.-% GPA. For shaping processes like pressure filtration the solid content as well as the rheological properties of the slurries are important because they strongly influence casting time as well as the green microstructure. This was investigated by recording of the stress/shear rate curves for solid contents up to 50 wt.-%. From these measurements a viscosity/shear rate diagram was calculated which is shown for different solid contents in Fig. 4. Suspensions containing up to 40 wt.-% n-TiN exhibit an ideal Newtonian flow behavior with viscosities between 2 mPa.s (20 wt.-%) and 5 mPa.s (40 wt.-%). A further increase of the solid content results in a non-Newtonian flow behavior. This shear thinning effect can be traced back to attractive particle interactions, which can cause an inhomogeneous microstructure during the forming step. From this point of view, pressure filtration experiments were carried out with a slurry containing 40 wt.-% n-TiN

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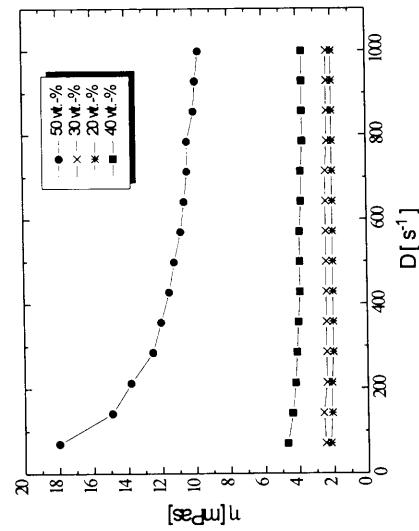


Fig. 4: Viscosity/shear rate diagram for n-TiN slurries with different solid contents.

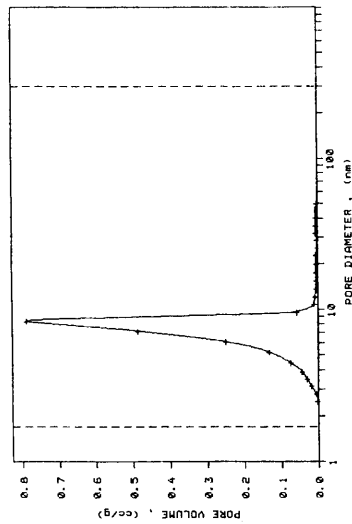


Fig. 5: Pore size distribution

In fig. 5 a typical pore size distribution of a n-TiN green body with a density of 50 % of theory is shown. The pore size of this sample ranges from 3 to 10 nm with an average pore size of 7 nm. The homogeneous packing of the nanoscale particles in green bodies could be further confirmed by high resolution SEM (Fig. 6).

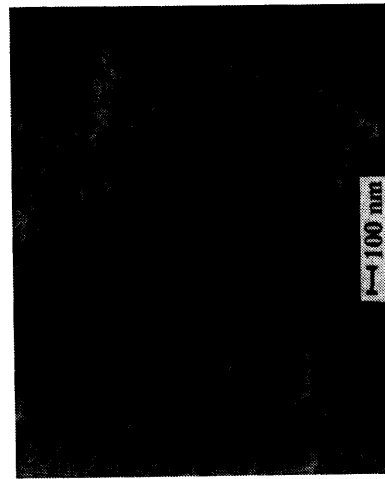


Fig. 6: Fracture surface of a green body (D = 0.50, High resolution SEM)

Nearly spherical TiN-particles with an average size between 30 and 40 nm are homogeneously arranged to each other forming a green microstructure without any voids significantly larger than the primary particle size. Solid content of 50 vol.-% are surprisingly high for nano scale sol-like slips. In conventional sol-gel processing with colloidal sol and comparable particle size maximum densities of 30 vol.-% are obtained.

The densification behaviour of green bodies was studied by dilatometer measurements. In Fig. 7 densification and grain growth vs. temperature are shown. For comparison the shrinkage curve of

a sample from a sub-micron TiN powder is given, too. Sintering of n-TiN already starts below 1000 °C and is finished around 1400 °C with a total linear shrinkage of 18 %. At this temperature a final density above 98 % is reached. In contrast, the specimen prepared from the coarser TiN powder (0.5 - 1 µm) has a much lower sintering activity with a neglectable shrinkage of 2 % up to 1600 °C.

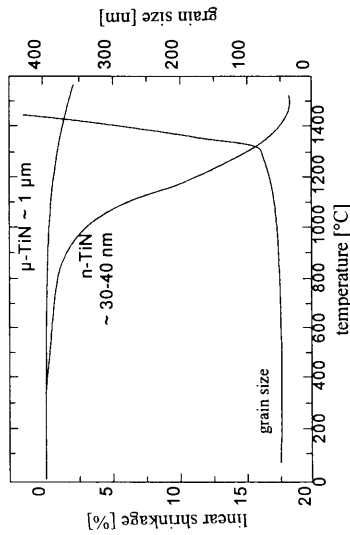


Fig. 7: Densification and grain growth of nano-scale TiN green compacts.

From fig. 7 it can also be seen that no significant grain growth has taken place up to 1200 °C, which corresponds to a sintering density of 96 % of theory. Accelerated grain growth was observed above this temperature, and a final grain size of 400 nm is obtained at 1400 °C. The low densification temperature clearly proves the high sintering activity of the powders.

CONCLUSION

The use of small organic molecules bound stable to the particle surface allows the preparation of well dispersed slips of high solid content from nano-scaled powders as demonstrated for n-TiN. This provides preparation of green samples without any packing irregularities of high green density which is a prerequisite for efficient sintering. Sintering experiments reveal that specimens can be densified without significant grain growth, which opens the opportunity for microstructure tailoring by post-heat treatment. Further investigations concerning densification and grain growth mechanisms are necessary to use the possibility of properties tailoring by annealing techniques.

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