Sintering of Aluminium Nitride Substrates for the Electronic Industry

A. Thimm* , F. Raether** , A. Klimera**, J. Ruska*

*   CeramTec AG, Marktredwitz, Germany
** Fraunhofer ISC, Würzburg, Germany

Abstract

AlN substrates of high quality can be sintered in different furnace types with firing programs adapted to the specific product requirements. Optically homogeneous and metallizable substrates with thermal conductivities of 180 W/(mK), bending strengths >360 MPa and deflections <0,3 % are produced in industry. The sintering of the AlN ceramics is investigated by means of in situ measuring methods. Phase changes are detected by High Temperature X-ray Diffraction and sintering shrinkage as well as thermal conductivity by a Thermooptical Measuring Method. Optimized sintering cycles are determined from the in situ measuring data and computer simulations. Segregations of the melt phase can be prevented by these methods.

Introduction

Aluminium nitride (AlN) ceramic is applied as substrate for heat sinks in the electronic industry due to its good thermal conductivity and its thermal expansion coefficient matching that of silicon. Besides power electronics AlN is used in highly integrated packaging techniques of microelectronics like multichip modules, where a high power density requires careful thermal management, as well as in special applications for cooling and heating elements. The thermal conductivity of high quality AlN ceramics is approx. 180 W/(mK) at room temperature. Impurities, which can be dissolved in the AlN lattice decrease the thermal conductivity drastically, because phonons are scattered at defects of the AlN lattice [1]. A pressureless sintering of AlN can only be obtained with sintering additives like Y_2O_3, which form a liquid phase at high temperature [2]. Commercially available AlN raw powders contain oxygen impurities of approx. 1 %, which have to be lowered to approx. 0,1 % during sintering [2]. This is achieved by a reprecipitation of the AlN at high temperatures via the liquid phase according to the so-called solution-reprecipitation mechanism. To

Corresponding author: Friedrich Raether, Fraunhofer ISC, Neunerplatz 2, D-97084 Würzburg, Germany, Phone: 00 49 (0) 931 4100 200, Fax: 0049 (0) 931 4100 299, E-mail : friedrich. raether@isc.fraunhofer.de

hold the oxygen, the liquid phase has to exhibit a lower oxygen activity than the AlN grains not yet reprecipitated [2]. Phenomena during AlN sintering have been investigated by in situ measuring methods and interpreted by thermodynamic models [3], [4], [5].

Substrates made of sintered AlN are requested with a thickness of 0,2 mm to 1,5 mm and in dimensions of 140 mm x 190 mm². The deflection has to be < 0,3 %. Furthermore, a bending strength of at least 360 MPa (measured by the four point bending test with a distance of support rollers of 40 mm, stress rollers of 20 mm and a sample width of 15 mm) as well as a high dielectric strength and a high electric resistance are required. A time-consuming post-processing of the substrates after the sintering process – e.g. by grinding – is usually not acceptable. Therefore after brushing, the substrates have to be sufficiently smooth. Local clusters of secondary phase or adhesions of separating agents must not appear on the surface. The substrates have to appear translucent and optically homogeneous. Variations in colour between different substrates are not acceptable. The substrates have to be suitable for further processing in different metallization processes, such as tungsten–glass metallization, noble metal–thick film metallization, DCB (Direct Copper Bonding) and – after a further surface treatment – thin film coating. Even with thin film coating polishing is not feasible for economic reasons.

In the following, processes for industrial production of AlN substrates are described and different heat treatments are discussed. Then the mechanisms which control the formation of microstructure during sintering are explained.

Production Process for AlN Substrates

Production of AlN substrates includes forming, heat treatment and finishing as well as a number of intermediate steps (Fig. 1). Most of the AlN raw materials are made from a carbo-thermal reduction or - cheaper – from direct nitridation. A slurry is made from the inorganic raw materials, i.e. a commercial carbothermal AlN powder and approx. 3 mass% of the sintering additive Y_2O_3 as well as organic additives. Then, tapes with widths of 800 mm and thicknesses between 0,25 mm and 1,80 mm are casted. After drying, the tapes are cut and stacked upon each other by a sepa-

rating agent (BN powder) evenly applied in six to twelve layers on firing batts made of BN. The firing batts have to withstand the high sintering temperatures of approx. 1800 °C and must not react with the AlN ceramics. A high purity of the BN batts is needed and especially the oxygen concentration has to be very low. The batts need a good dimensional stability with a planarity better than 0,2 %. For economic reasons they have to withstand far more than 100 sintering cycles. A mechanical treatment of the BN batts between the firing cycles is required, to remove shivers or cakings of the melt phase.

Debinding of green compacts is performed thermally at maximum temperatures between 600 °C and 700 °C – using an air flow, to avoid residual carbon in the parts. The carbon would cause colorings and deteriorate sintering kinetics and planarity of the substrates. Vice versa, the kiln run must not be ignited by a too strong flow of air and BN as well as AlN must not be oxidized. The pyrolysis has to be performed very homogenously, to assure that the substrates do not warp. I.e., the organic additives have to be adjusted to the requirements during debinding.

Sintering is done in nitrogen atmosphere with stacks, alternately built up out of AlN substrates and a BN firing batt. It can be carried out continuously or in batch mode - in furnaces with tungsten or molybdenum heating units as well as in graphite furnaces. Regarding tungsten/molybdenum furnaces, metal contaminations on the substrates have to be carefully avoided, as they also cause darker colorings. The quantity of the sintering additive (Y_2O_3) has to be adjusted to the furnace type: For tungsten/molybdenum furnaces generate a less reducing atmosphere than graphite furnaces, more additive is required, to reach the same final composition within the secondary phase. The smaller furnace capacity and the lower maximum temperature are serious disadvantages of the tunsten/molybdenum furnaces, compared to the graphite furnaces. The latter limits the possibilities for an optimization of the firing conditions considerably. E.g., AlN made from direct nitridation cannot be sintered in the tungsten/molybdenum furnaces to the required translucency. In graphite furnaces an additional protection of the AlN against the reducing furnace atmosphere is required. For that, either coated graphite or BN are used. Several enclosures may be necessary, to avoid colourings at the edges of the substrates or warping by reducing furnace gases. On the other hand, a homogenously reducing atmosphere is advantageous, because it contributes to the removal of the oxygen impurities in the AlN powder.

Hood-type graphite furnaces have proven to be well appropriate. They are available with the required dimensions and temperatures up to 1850 °C and need little maintenance. Typical sintering temperatures are between 1750 °C and 1780 °C and hold times are between 3 h and 7 h. The firing cycles have to be adjusted to the requested substrate thickness and the specific demands of the products. Higher temperatures and longer hold times improve the thermal conductivity of the AlN substrates, because the secondary phase is being reduced more intensely and thereby its oxygen activity is decreased. However, strength decreases at a longer hold time, because grain growth starts and homogeneity of the microstructure decreases. In addition, melt phase may exude at the surface, if the hold time is too long (Fig. 2). This would deteriorate the sub-
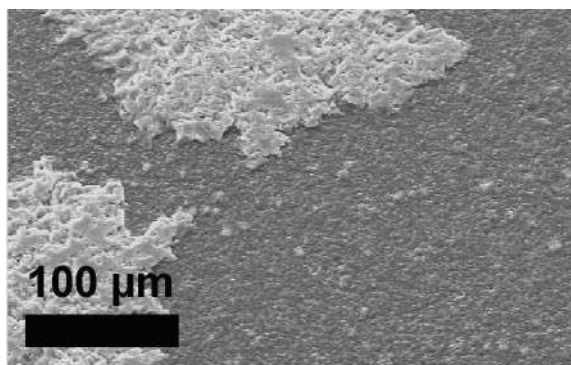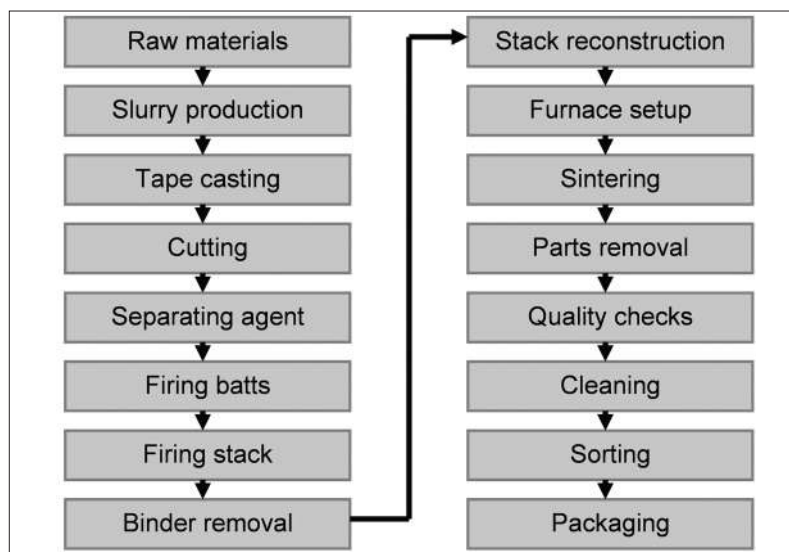

Fig. 1 (above) Process flow at the production of AlN substrates

Fig. 2 (right) Surface of AlN substrate after firing showing clusters of secondary phase
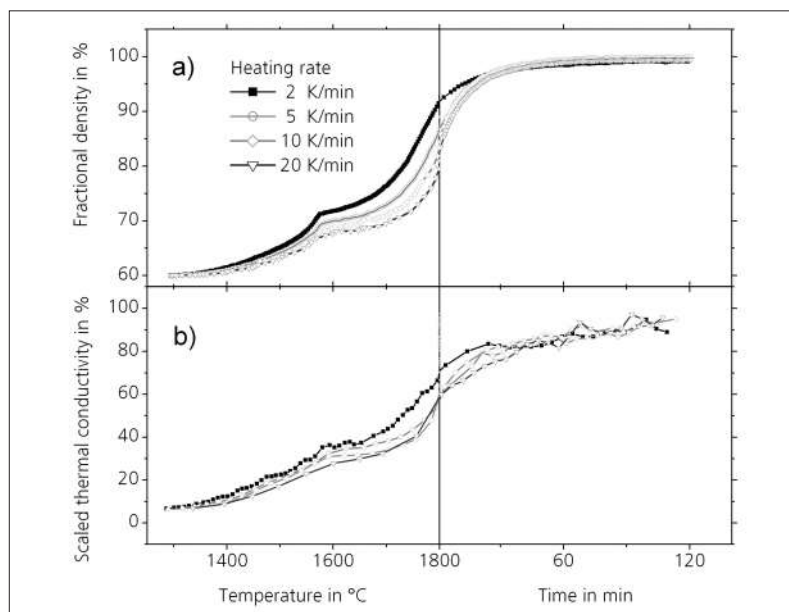

Fig. 3 In situ investigations at AlN samples with 3 % Y_2O_3: Development of fractional density (a) and scaled thermal conductivity (b) during sintering

sequent metallization processes. The process window to produce AlN substrates of good translucency, thermal conductivity and strength is very narrow. Temperature tolerances are smaller than ±3 K at sintering temperature. The cooling process at the end of the hold time has to be carried out effectively and precisely, to prevent segregation of the melt phase.

Mechanisms during AlN Sintering

At heating up to 1100 °C the sintering additive Y_2O_3 reacts with the thin Al_2O_3 impurity layer, located at the surface of the AlN particles. Thereby, crystalline yttrium aluminate phases [6] are formed. These are detected directly using a high temperature X-ray diffractometer [3]. Sintering shrinkage starts at 1300 °C. Shrinkage was determined non-contact by a so-called thermooptical measuring system (TOM) [4]. To provide a very clean furnace atmosphere is the precondition for a successful in situ measurement of the AlN sintering [5]. Fig. 3 shows shrinkage curves during heating of AlN green compacts in a graphite furnace [5]. An activated solid phase sintering takes place between 1300 °C and 1600 °C, during which AlN is transported via the solid yttrium aluminates. The yttri-

Fig. 4 Shape of AlN grains after minimising interface energy for different dihedral angles: left 120° and right 75° (melt phase volume 5 %)

Fig. 5 Secondary phase in model (left) and SEM image of the secondary phase after removal of the AlN phase by etching (right)

Fig. 6
Interface energy depending on melt phase fraction and dihedral angle

um aluminates melt at 1600 °C, which was measured by high temperature X-ray diffraction [3]. Shrinkage above 1600 °C is controlled by liquid phase sintering. I.e., the AlN dissolves preferentially at the grain contacts and is precipitated at the surfaces of the AlN grains. Due to this reprecipitation the pore volume is decreased, until the porosity almost disappears after a hold time of 30 min. at 1800 °C (Fig. 3a).

Simultaneously the heat transport inside the AlN samples was measured by TOM. For that, the well-known laser-flash method [7] has been modified, to determine the thermal diffusivity of ceramic samples during sintering [4]. The thermal diffusivity α was converted into thermal conductivity λ by appropriate scaling with the corresponding data measured for a dense sample at the respective temperature T (Fig. 3b):

$$\lambda \;=\; c_p\,\rho\,\alpha \; ;$$

$$\lambda_{scaled} \;=\; \frac{\lambda(T)}{\lambda_{dense}(T)} \;=\; \frac{\rho(T)\,\alpha(T)}{\rho_{dense}(T)\,\alpha_{dense}(T)} ; \qquad (1)$$

with c_p = specific heat and ρ = density.

Scaled thermal conductivity increases similarly to the density of the AlN samples during heating (Fig. 3b). It further increases during the hold time, also after the final density has been achieved. During cooling of the AlN samples after sintering, it has been detected by high temperature X-ray diffraction, that the melt phase solidifies at temperatures of approx. 1700 °C and yttrium aluminate phases are formed according to the phase diagram [3].

An extended hold time leads to a further reduction of the melt phase, to a decrease of its oxygen activity and thereupon to a decrease of the oxygen concentration inside the AlN grains, caused by further reprecipitation and grain growth. I.e., the thermal conductivity of the sintered AlN ceramics increases. However, the wetting conditions between melt phase and AlN also change. These wetting conditions control both, exudation of the melt phase at the surface and a possible segregation inside the ceramic [5]. The relevant property is the dihedral angle Θ, which is defined by the ratio of the grain boundary energy E_{GB} of the AlN grains and the interface energy E_{SL} between melt and AlN:

$$\cos\,(\Theta/2) = \frac{E_{GB}}{2\,E_{SL}} . \qquad (2)$$

Fig. 4 shows a microstructure model, which was applied for the simulation of the interface energy [5]. The plane grain boundaries between the AlN grains are grey colored and the interface between AlN and liquid phase is displayed by a Finite Element mesh. The model uses a tetrakaidecahedron as unit cell, which can be arranged space filling in a three-dimensional lattice. Moreover, it has 14 faces which fits to the number of nearest neighbors in sintered ceramics. The interface between AlN and melt phase was varied for each structure, until the interface energy was minimal. For the minimization the computer code Surface Evolver [8] was combined with in-house software. The microstructures obtained from the model represent the real microstructures of the AlN ceramics quite well (Fig. 5). The model structures and the respective interface energies have to be recalculated for various concentrations of melt phase und different dihedral
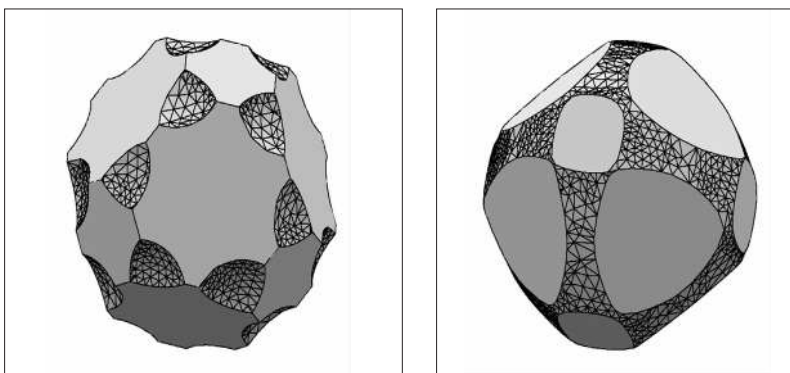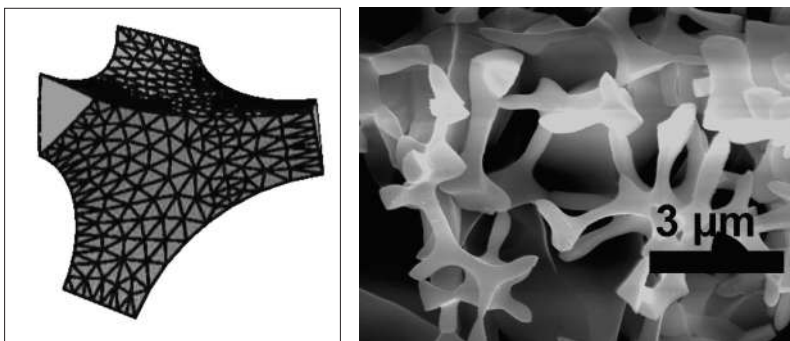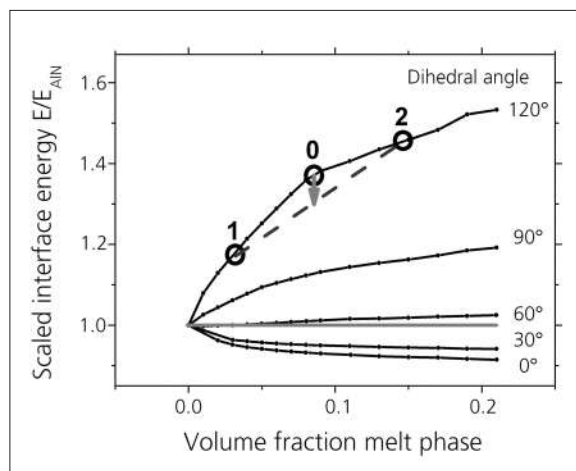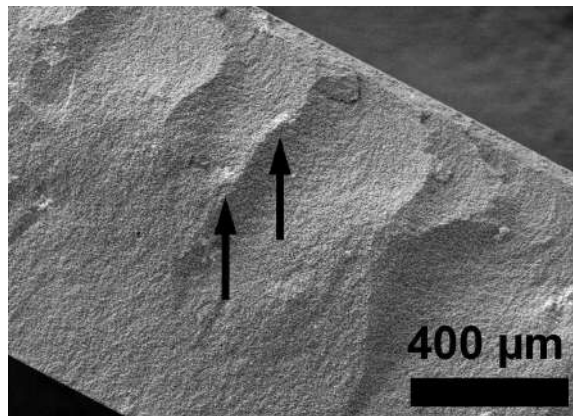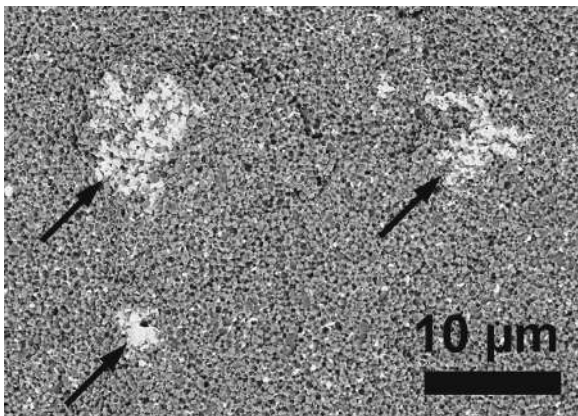
Fig. 7
SEM images of a sintered AlN ceramic with clusters of secondary phase (arrows): polished section (left) and fracture surface (right)

angles. Fig. 6 shows a summary. (Interface energies are scaled by the interface energy of an AlN ceramic, which is completely free of melt phase, i.e., which only contains grain boundaries). The scaled interface energy for dihedral angles above approx. 60° is >1. It will be decreased, if melt phase and AlN are separated completely. Thus, a thermodynamic driving force for a macroscopic decomposition exists. Another phenomenon can be identified from the course of the interface energy curves in Fig. 6: The concave shape of the curves at dihedral angles above 60° also causes a decrease of the interface energy by local segregation. This is denoted by the line between points 1 and 2. If a melt phase, which was homogeneously distributed at the beginning (point 0), will be redistributed, as to form a region with lower (point 1) and another region with higher melt phase concentration (point 2), the total interface energy will be decreased according to the lever rule known from the construction of phase diagrams. The energy decrease is indicated by the arrow facing downwards (Fig. 6). As a result, there is a thermodynamic driving force towards local segregations for dihedral angles above 60°. In fact, such segregations have been detected in the scanning electron microscope (SEM). Fig. 7a shows a polished section of sintered AlN ceramic. Local accumulations of the secondary phase are visible by the light contrast of the yttrium. These clusters are marked by arrows. (Samples which were quenched immediately after final density was achieved did not show any segregation. I.e., inhomogeneous green parts could be excluded as reason for the cluster formation). Fig. 7b shows a fracture surface with clusters which cause a deflection of the fracture front. The secondary phase has a higher coefficient of thermal expansion than the AlN [9]. Therefore, tensile stresses occur at the clusters during cooling-down, which deteriorate strength of the ceramic.

It is concluded, that dihedral angles above 60° have to be avoided during sintering. To keep this condition is difficult, because the dihedral angle cannot be measured directly in situ. As shown by microstructure investigations with samples at ambient temperature, the dihedral angle changes during cooling down [10]. Thus, measuring at quenched samples can falsify the high temperature properties. Instead of the dihedral angle, thermal conductivity can be used as in situ measurable quantity, to get indirect information about the wetting properties. This is related to the fact that the thermal conductivity of the melt phase is lower by an order of magnitude than the thermal conductivity of the AlN [5]. A wetting melt phase penetrates into the

grain boundaries and forms a thermal resistance, whereas a non-wetting melt phase just exists in isolated pockets or channels at the grain corners or edges. Therefore, thermal conductivity should decrease with decreasing dihedral angle. This correlation was also confirmed quantitatively by a Finite Element simulation of the heat transport in the model structures [5].

In situ measurements of the thermal conductivity of AlN samples, which were sintered already, showed two effects which are important for the understanding of microstructural changes at high temperatures: First, the scaled thermal conductivity decreases with increasing temperature [5] and second, it increases with increasing sintering time at constant temperature (compare also Fig. 3b). The first is attributed to the increasing weight of entropy with increasing temperature which favors the disordered solid-liquid interface. The second is explained by grain growth which favors low energy grain boundaries and thereby decreases the numerator in equation (2).

From the changes of dihedral angle it is concluded, that a short holding time at the highest reasonable temperature should lead to optimal sintering results. An upper limit is given by the decrease of thermal conductivity when very high sintering temperatures above 1900°C are applied. This decrease is attributed to the formation of Al_2OC impurities in the AlN lattice [11]. Using the high temperature hold time, its end point has to be kept precisely and cooling down has to be effected quickly, because otherwise the ceramics become thermodynamically instable and a local and macroscopic segregation of the melt phase occurs.
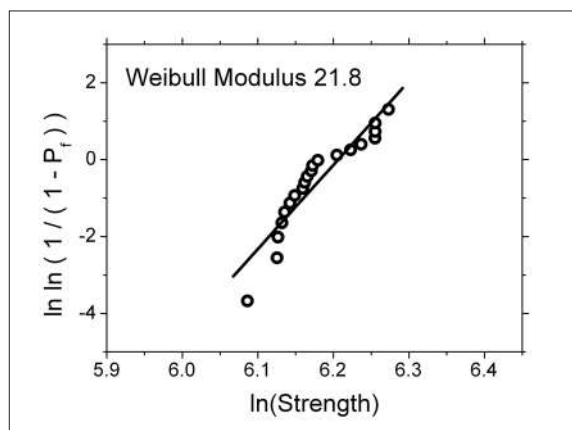

Fig. 8 Weibull plot of strength measurements (4 point bending test) at AlN substrates
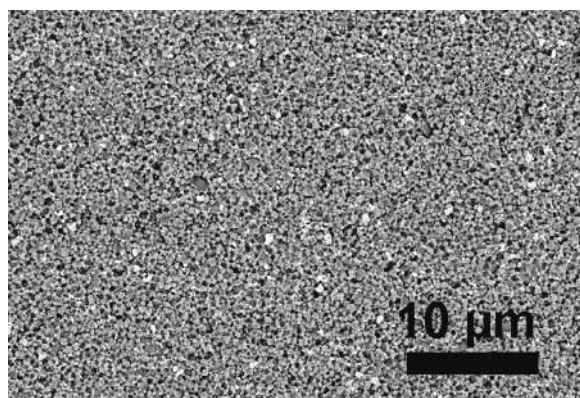
Fig. 9 Polished section of an AlN ceramic after optimised sintering

From the FE simulations, it was concluded also, that strength and thermal conductivity of the AlN ceramics can be improved furthermore, if the secondary phase will be removed from the AlN grain boundaries [5]. During cooling down of the AlN ceramics, the increase of the dihedral angle with decreasing temperature can be used to precisely adjust the desired microstructure.

Summary

Compared to standard sintering cycles, strength has been improved by approx. 25 %. Weibull modulus of the ceramics increased from 12 to 22 (Fig. 8). The improved mechanical properties are attributed to a homogeneous microstructure of the ceramic. Fig. 9 shows the microstructure of a sintered AlN ceramic, after optimisation of the firing cycle. Segregations are eliminated completely which confirms the model presented in the previous chapter. It is assumed that other ceramics sintered by a liquid phase mechanism can be optimized by the same strategy. Recently also improved mechanical properties were obtained using a holding period at lower temperature where the Weibull modulus was 17 and strength was only 10 % less than with the high temperature holding period.

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