Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of the European Ceramic Society 23 (2003) 1997–2004
www.elsevier.com/locate/jeurceramsoc

Effect of surface silanisation on the dry pressing behaviour of silicon nitride powder

Siegfried Vieth[a,*], Marietta Uhlmann[a], Dietmar Linke[a], Ulrich Klemm[b], Dieter Sobek[b], Floriana-Dana Börner[b]

[a]*Brandenburgische Technische Universität Cottbus, Fakultät 1, LS Anorganische Chemie, Karl-Marx-Str. 17, D-03044 Cottbus, Germany*
[b]*Technische Universität Dresden, Institut für Werkstoffwissenschaft, Universitätsprofessur für Anorganisch-Nichtmetallische Werkstoffe (Technische Keramik), Mommsenstr. 13, D-01062 Dresden, Germany*

Received 10 June 2002; received in revised form 4 December 2002; accepted 8 December 2002

Abstract

The influence of surface modification of silicon nitride powders with alkylsilanes on their compaction behaviour was studied with an instrumented compacting tool. The powder–powder interactions were investigated by viscosity measurements additionally. All silanes, even those with short alkyl chains, reduce interparticular interactions (e.g. hydrogen bridging) and therefore improve the compaction behaviour of ceramic granules in general.

Keywords: Pressing; Silane modification; Si_3N_4

---

1. Introduction

Surface modification of silica powder with silanes is a well established method for the preparation of stationary phases for chromatography purposes. The silanes react with surface OH-groups. As a result, a stable, covalent bond between powder surface and modifying group is formed.[1,2]

Usually, silicon nitride powder is covered by a thin silica layer.[3] Therefore, it is also suitable to silanisation reactions. However, the described methods for these reactions are adopted to common ceramic processing and not to chemical requirements (e.g. exclusion of water),[4–7] For this reason, the surface characteristics of the obtained powders are uncertain. Furthermore, a deterioration of the quality of green bodies can be observed.[8]

Our method of powder silanisation[9,10] is very similar to the synthesis of modified silicas for chromatography purposes[1,2]—usage of an inert solvent, exclusion of water, and the addition of a catalyst such as pyridine. As a result of such a process, the silane is covalently bound to the powder surface. Due to the application of "stoichiometric" amounts of silanes (with respect to the surface capacity), monolayers of modifying groups can be assumed.[9,10] Surface properties of silicon nitride powder can effectively be controlled by silanisation. Therefore, the dry-pressing behaviour of granules made of silanised powders is interesting both from the scientific and technological point of view.

An instrumented press is a versatile tool which allows the in-situ measurement of relevant process parameters during powder compaction. With the aid of this device, a detailed evaluation of compressibility and compactibility of ceramic granules, including an estimation of friction conditions, is possible.[11–13] Thus, the in-situ investigation of silane-modified silicon nitride powders should allow new insights into the compaction process.

2. Materials and methods

Silicon nitride (UBE-10) powder is attrition milled[14] in heptane in the presence of different silanes[9,10] leading to granules **2–4** (Fig. 1). The amount of the silanes used

---

* Corresponding author.
E-mail address: svieth@tu-cottbus.de (S. Vieth).

0955-2219/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0955-2219(03)00021-9

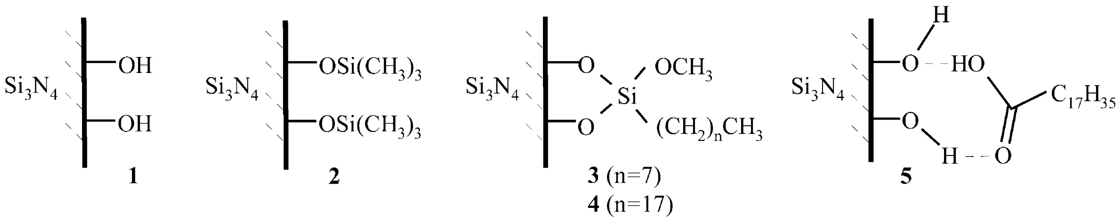
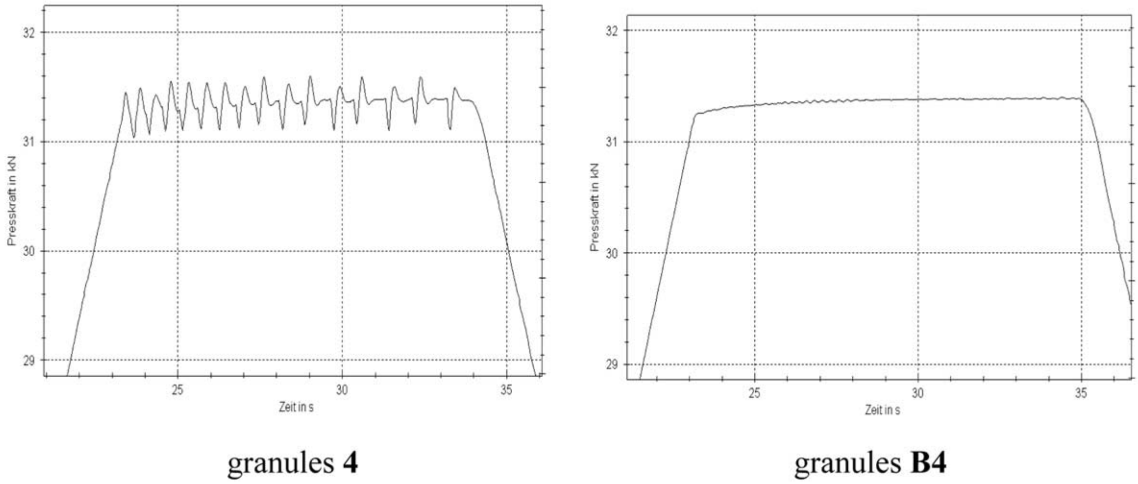


Fig. 1. Silicon nitride powders investigated.



granules **4** granules **B4**

Fig. 2. Enlarged part of the course of the upper punch force during the holding period.

is 0.12 mmol/g, leading to a monomolecular layer of modifying groups on the powder surfaces[9,10]

In Table 1 all granules examined in the study are summarized. All modified materials further marked with the letter B and the batch number contain additionally 5% binder (polypropylenglycole) and 1% lubricant (stearic acid) which are added at the end of the milling process. After the removal of the solvent (80 °C, vacuum), the powders were granulated by rolling granulation.[15]

Viscosity measurements were performed on a rotation viscosimeter RHEOTEST 2 (cylindric set up, Fa. RHEOTEST, Medingen).

The compaction behaviour of granules was investigated with an instrumented compacting tool.[11–13] Primary measured parameters are the forces at the top punch (F_1), and at the bottom punch (F_2), the radial stress on the die wall (σ_R) and the distance covered by the top punch during compaction. Die and bottom punch are fixed. This device allows to derive numerous important process parameters, e.g. pressure–density relationships and the distribution of the applied pressure in axial and radial directions. The parts of plastic and elastic deformation as well as friction and energetic parameters can be calculated. All experiments were performed with a compaction pressure of 100 MPa.

Table 1
Granules investigated in the study (see also Fig. 1)

No.	Modifier	Lubricant
1	–	–
2	$(H_3C)_3Si–NH–Si(CH_3)_3$	–
3	$(H_3CO)_3Si–C_8H_{17}$	–
4	$(H_3CO)_3Si–C_{18}H_{37}$	–
5	–	$C_{17}H_{35}–COOH$

3. Results

3.1. General compaction course

In the case of high friction losses at the die wall so-called stick–slip-mechanisms can be observed (Fig. 2). This process is usually connected with loud noises during pressing: At certain points the compaction of the granules does not progress, although an increasing pressure is applied. As a result of the combination of high radial stress and wall friction coefficient, the material sticks. After a further increase of pressure a sudden compaction progress takes place till the material sticks again and again with changing frequency and amplitude. Stick–slip processes should be avoided, because they are the reason for macroscopic defects in the green bodies and enhance the wear of the pressing tool. The lack of a lubricant (stearic acid) in the granules **1–4** causes distinct stick–slip effects whereas all types with binder and lubricant exhibit a compaction without

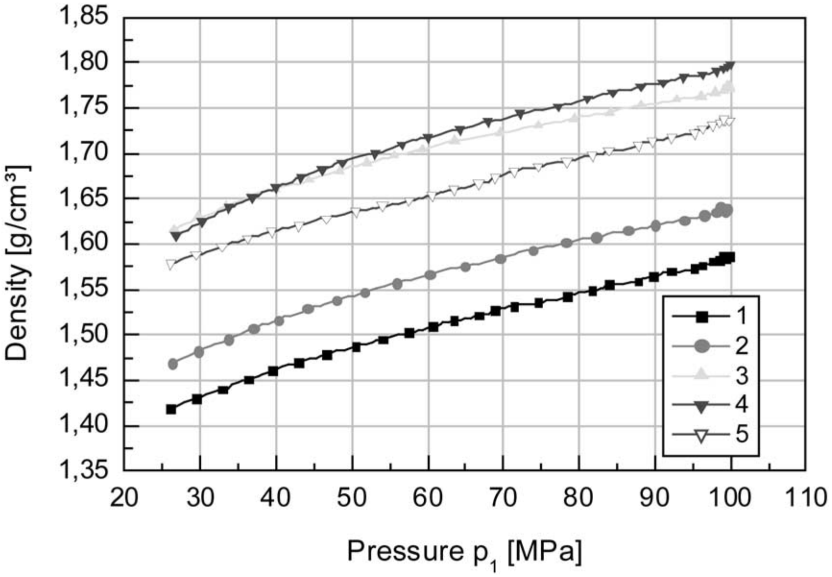


Fig. 3. Dependence of the green density on the pressure for granules **1**–**5**.

inhomogeneities—as well as granules **5**. The best result (almost no heterogeneities in the compaction curve) is obtained with batch **B4**. Both the lubricant and the modification with a long-chain alkyl silane improve the compaction behaviour.

3.2. Compressibility

Compaction experiments with the granules **1**–**5** reveal very clearly the improved compressibility of silanised powders (Fig. 3). The strongest effect can be recognized if long-chain alkyl silanes are used (granules **3** and **4**). Granules **5**, containing the same stoichiometric amount of stearic acid alone, are less effective. If granules with binders and lubricants (B-types) are compared, the effect of silanisation is even clearer (Table 2). Also less effective silanes (as in type **B2**) yield higher green densities than granules containing only stearic acid (granules **B1**).

Table 2
Relative green densities of granules **B1–B4** (in% th. d.) after a pressure of 100 MPa

Granules No.	At pressure	After unloading
B1	50.7	49.4
B2	52.9	51.3
B3	55.0	53.4
B4	58.3	56.0

3.3. Friction-related parameters, stress-gradients

Friction processes during compaction have a significant impact on all properties of the green body.[11–13] The results obtained from the granules **1--5** show the effect of powder silanisation on friction parameters very clearly. Powder–wall friction as well as powder–powder friction can be diminished by silanes. The longer the alkyl chain the smaller the appropriate coefficents (Table 3). A comparison of granules **4** and **5**—both powders are treated with organic compounds of the same chain length—reveals distinct differences between silanisation and lubrication. The most important result of the silanisation experiments is the proved possibility of changing the powder friction coefficient to a large extent. With conventionally used organic additives such a broad variation is impossible. Thereby the octadecylsilane causes the strongest reduction of μ_P (Fig. 4) followed by the highest densities.

Table 3
Friction related parameters of the compaction process

Granules	**1**	**2**	**3**	**4**	**5**	**B1**	**B2**	**B3**	**B4**
μ_W	0.885	0.799	0.431	0.369	0.153	0.166	0.202	0.172	0.155
μ_P	0.460	0.403	0.371	0.328	0.366	0.418	0.390	0.342	0.296
F_E (kN)	2.80	5.07	2.39	2.69	1.00	1.25	1.17	0.94	0.81
F_2/F_1 *(%)	22.5	23.5	44.6	47.8	73.9	72.7	67.9	71.1	73.1

μ_P: friction coefficient (powder-powder); μ_W: friction coefficient (powder-wall); F_2/F_1: force transmission quotient; F_E: ejection force.

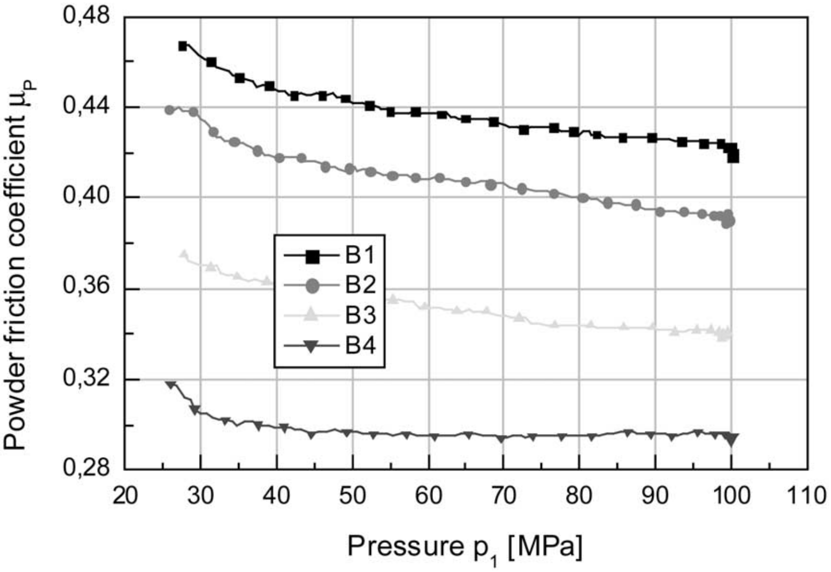


Fig. 4. Dependence of the powder friction coefficient on the pressure for different modifications of powders.

The effect of the silanisation on all parameters which are influenced by wall friction processes is rather poor. The presence of stearic acid in the B-types leads to force transmission quotients and wall friction coefficients which are common for powder compaction processes by uniaxial pressing.

The ejection force F_E is a measure for the static friction of the green compact at the die wall. Here, only the addition of stearic acid shows a significant diminishing effect for granules **1–5**. Octyl and octadecyl silane have almost no influence (**3**, **4**). The smaller trimethylsilyl group even leads to increased values (**2**). All B-types show very small values, an influence of the kind of silanisation agent can be seen.

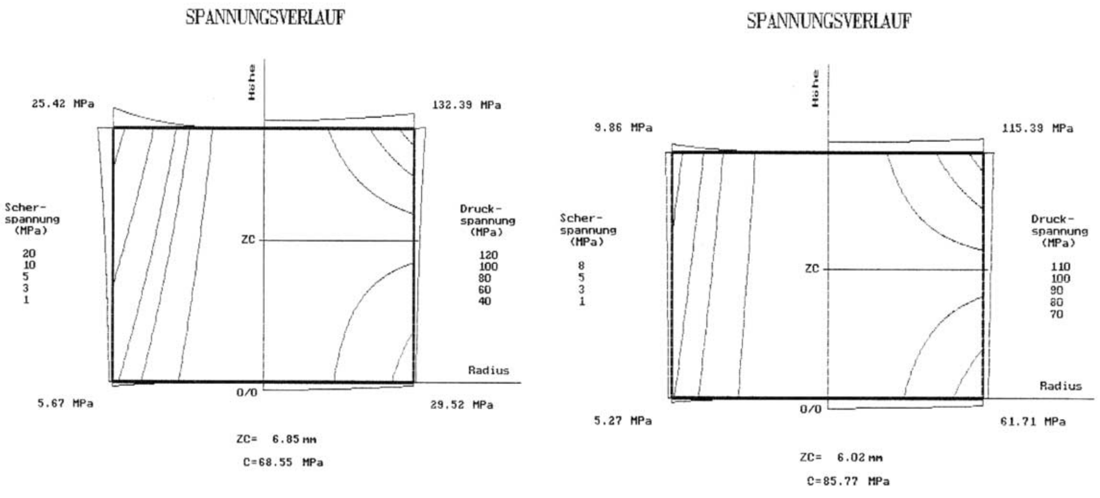
Force transmission F_2/F_1 (Table 3) is strongly related to density gradients along the pressing direction on the one hand and to powder–wall-friction processes on the other. Therefore, the dependence of F_2/F_1 on stearic acid addition or silanisation can be derived from the friction coefficient dependence. Thus, lubricant addition, e.g. stearic acid, is a prerequisite for low axial density gradients.

Density differences within the green body cause irregular shrinkage rates during the sintering process. Using a compaction model created by Thompson,[16] which was modified on account of own experimental results, distribution of shear and pressure stresses can be estimated from friction-related parameters. From these calculations, also taking the elastic relaxation into consideration, the density distribution in the green body after ejection can be shown.[17] This model was verified by X-ray computed tomography. In the worst case (granules **1**) the axial stress difference reaches an extent of nearly 120 MPa. Stresses can be reduced significantly by stearic acid additions. Silanisation is of limited influence. For this reason, reduction of powder–wall friction is most important for the reduction of absolute values and stress differences. Fig. 5 shows the stress distributions within green compacts of octadecylsilyl-modified granules **4** and the corresponding type with organic additives (**B4)** respectively.

3.4. Elastic relaxation

By removing the pressure, the so-called spring back or elastic relaxation of the green body takes place as an unwanted, but generally observed phenomenon. In particular when a large part happens outside the die, this spring back can be the cause of development of macroscopic defects like cracks or laminations.[11–13] The method of instrumented compacting allows the measurement of the total amount of spring back and the parts inside and outside the die (Table 4). Regarding the granules **1–5**, silanes as well as stearic acid increase the total axial relaxation by about 1%. For granules **1**–**4** the share of springback outside the die is higher. The corresponding green bodies often show the mentioned end-capping and lamination effects (Fig. 6). In particular compacts of granules **2**, exhibiting large stress values, show such a behaviour. Silanisation with octyl or octadecyl silane (granules **3**, **4**) has only a restricted positive effect. The impact of stearic acid (granules **5**) is much higher.

Types **B1**–**B3** yield smaller b/l values, compared to the granules without binder and lubricant (**1**–**3**). Granules **B4** exhibit values similar to the appropriate granules **2**–**4**, showing that the compaction potential of these types is utilized to a large extent. This is confirmed by the high force-transmission coefficents of these granules (Table 3). In general, the absolute amount of spring



granules **4**

granules **B4**

Fig. 5. Stress distribution in green compacts (in each case at the left side shear stress and at the right side pressure stress).

Table 4
Spring-back behaviour

Sample	**1**	**2**	**3**	**4**	**5**	**B1**	**B2**	**B3**	**B4**
b/l (%)	2.97	3.99	4.00	4.00	4.13	2.17	2.94	2.51	4.18
b_i/b (%)	64.1	62.8	65.4	66.1	78.2	78.6	77.6	85.8	87.8
b_o/b (%)	35.9	37.2	34.6	33.9	21.8	21.4	22.4	14.2	12.2

l: length of cylindrical green body; b: total spring back; b_i: spring back inside the die; b_o: spring back outside the die

back increases with the degree of compaction. Here, an advantage of modified granules becomes obvious: Compared to unmodified granules, a lower pressure is necessary to obtain the same green density, combined with a lower degree of spring back.

Turning from granules **1–5** to types with binder and lubricant **B1–B4** the ratio of inner to outer relaxation is improved due to the presence of stearic acid. Regarding the silanized types **B2–B4**, b_i/b_o ratio increases with the chain length of the silane. In particular, batches **B3** and **B4** exhibit very low values for b_o/b. As it can be seen in Fig. 6, especially octadecylsilyl-modified granules (**B4**) allow the preparation of green compacts in a high quality.

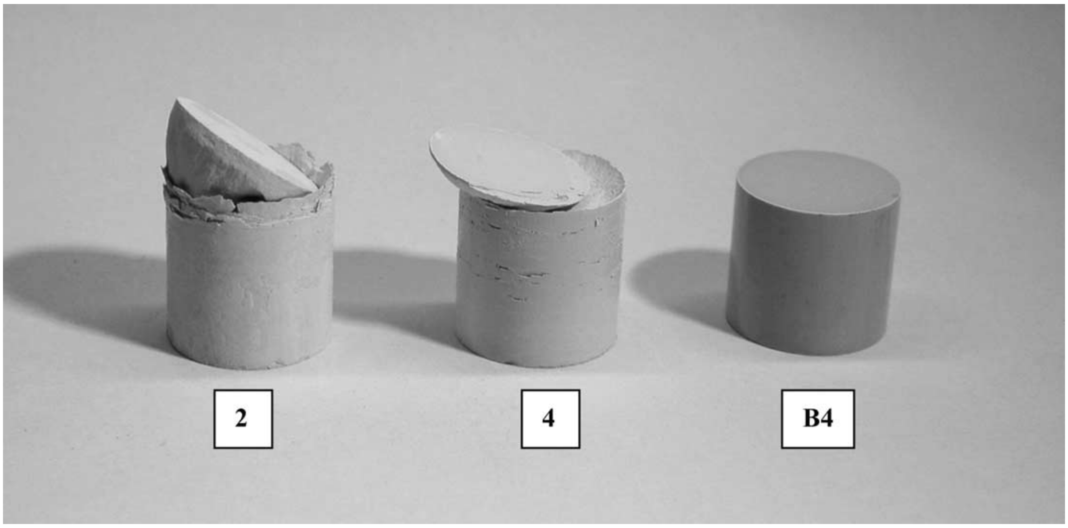


Fig. 6. Green bodies from modified granules **2** and **4** and from type **B4**.

Table 5
Energy and strength parameters

Granules	1	2	3	4	5	B1	B2	B3	B4
W_1 (Nm)	12.60	11.34	7.85	8.67	4.14	5.83	5.59	5.78	5.22
W_2 (Nm)	4.00	2.18	3.79	5.26	8.05	11.09	7.73	8.97	9.45
W_2/W_T (%)	23.0	14.9	30.5	35.8	61.5	62.4	54.6	57.7	61.0
σ_{DC} (MPa)	–	–	0.16	0.29	0.48	0.78	0.52	0.50	0.54

W_1: friction energy; W_2: energy uptake; W_T: total compaction energy; σ_{DC}: diametral compressive strength.

3.5. Energy parameters and strength

The registration of punch forces as a function of the top-punch distance provides different energy parameters[11–13] (Table 5). Silanisation generally diminishes friction energy W_1, but not as effective as stearic acid. Stearic acid is the only additive which can effectively reduce powder-wall friction (see above). Therefore, powder–wall friction contributes in a much higher degree to friction energy than powder–powder-friction does.

As experienced in earlier experiments,[11–13] energy uptake W_2 makes a contribution to green density and strength. As Table 5 shows, there is a tendency for modified B-type granules that their compaction results in smaller W_2 values. The effect of silanisation on energy uptake is more obvious, if W_2 values are estimated for a certain green density, what can be seen from dynamically recorded force-way-graphs (Fig. 7). Already the small trimethylsilyl as well as octylgroups lead to a lower energy uptake compared to unmodified granules with an even higher 3.4% content of stearic acid (marked as **B5** in Fig. 7). Generally the energy uptake related to a constant density decreases with increasing chain length of the silane.

As mentioned above and well-known from previous studies[11–13] a high value of W_2 for a given pressure corresponds to high strength of the green compact. The results compiled in Table 5 confirm this connection. Silanisation reduces the energy uptake W_2 and also the strength σ_{DC}. Nevertheless, green bodies from granules **B2**–**B4** definitely have a sufficient strength for typical handling procedures. Perhaps, this tendency of strength reduction is partially compensated by the higher degree of compaction.

Another immediate advantage of silanisation can be derived from the fact that it is possible to reduce the required pressure for the desired density. That means that the danger to get into the region with prevailing elastic deformation (the so-called "overpressing") and as a consequence the development of macroscopic defects in the compacts decreases essentially.

4. Discussion

Table 6 summarizes the results discussed above. Obviously, silanes and stearic acid differ in their influence on compaction behaviour and hence on properties of green bodies. Stearic acid significantly reduces pow-

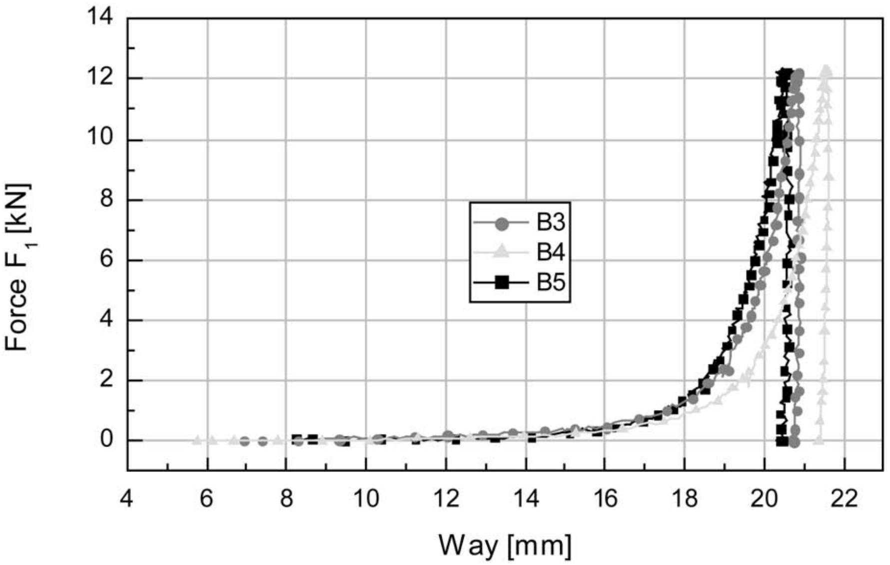


Fig. 7. Characteristic force–way-graphs for granules with binder and lubricant.

Table 6
Influence of silanisation and lubricant addition on properties of the green bodies

	Green density	Density gradients	Total springback	Fraction of spring back inside the die	Green strength
Silanisation	Distinctly increasing	Weakly decreasing	Weakly increasing	Weakly increasing	Weakly decreasing
Stearic acid addition	Weakly increasing	Distinctly decreasing	Weakly increasing	Distinctly increasing	Increasing

der–wall friction and has a positive effect on properties which are influenced by this process, e.g. density gradients. However, the effect on green density is rather poor. Green density correlates with parameters which are related to powder–powder interactions. The reduction of the corresponding friction coefficent μ_P and of related energy uptake causes an increase in green density.

Our experiments show, that all parameters which are related to powder–powder interactions are significantly influenced by silanisation. Long chain alkyl silanes (e.g. granules **4**, **B4**) exhibit the most distinct effects. They tremendously reduce the powder-friction coefficient μ_P, the related energy uptake W_2 and also the viscosity of Si_3N_4-suspensions in unpolar solvents (Table 7). On the other hand, silanes cannot reduce the powder-wall friction effectively, and even the octadecylsilane (granules **4**) exhibits an insufficient impact if compared to stearic acid (granules **5**).

Both lubricant and silane bind to surfaces and cause effects known as steric stabilisation or boundary lubrication.[18,19] However the obtained results indicate differences in the binding strength to Si_3N_4-powder surfaces. Obviously, alkylsilanes are bound much stronger than stearic acid. Simple elution experiments support this thesis (Table 8). The octadecylsilyl group of granules **4** withstands boiling in ethanol, whereas the stearic acid of granules **5** is largely removed.

Due to the preparation conditions used, the strong fixation of silanes to the powder surface is best explained by a covalent bond.[1,2] The silanes used carry hydrophobic groups. By alteration of OH groups of powder **1** to alkylsilyloxy groups (powders **2**–**4**, see Fig. 1), they turn the polar surface of silicon nitride powder to a non-polar state. For instance, powder **1** (“common” Si_3N_4-powder) gives stable suspensions in aqueous media, whereas the silanised powders **2–4** can be suspended only in organic solvents.[9,10] Polar interactions (dipol–dipol interactions, hydrogen bridging) are much stronger than the interactions between non-polar moleculs or particles which are only bound due to van-der-Waals forces. Therefore, silane modification effectively reduces powder–powder interactions. Due to the binding strength, alkylsilyl groups can withstand shearing forces and are still efficient in flowing powder suspensions and during powder compaction. Hence, silanised powders cause lower suspension viscosities and higher green densities. The effect is particularly distinct if the octadecylsilane (granules **4**, **B4**) is used.

No evidence was found in the literature for a covalent binding of carboxylic acids to silica or similar solids. Hence, the fixation of stearic acid to the powder surface is weaker. Compared to silanes, it can be desorbed much easier from the powder surface—by elution (Table 8) as well as by shearing forces. Insufficient shielding is the consequence, causing intensive powder–powder interactions and low green densities. During viscosity measurements the shearing forces are weaker compared to dry pressing. Hence, stearic acid also reduces the viscosity of powder suspension—but less effective than the octadecylsilane.

Due to the stable immobilisation, silane modification reduces powder–wall friction only slightly. Here, the weaker fixation of stearic acid is an advantage. This substance leads to a more effective lubrication of the die wall, as the low friction coefficients μ_P and ejection forces F_E show.

Table 7
Influence of surface modification of Si_3N_4-powder on dry pressing and rheologic behaviour

Granules	Viscosity (mPa. s) at a shearing rate			μ_P
	$D_S = 80\ s^{-1}$	$D_S = 220\ s^{-1}$	$D_S = 365\ s^{-1}$	
1	[a]	[a]	[a]	0.460
2	[a]	[a]	[a]	0.403
3	66	31	21	0.371
4	28	13	9	0.318
5	148	61	40	0.366

μ_P: friction coefficient (powder-powder)

[a] Suspension is instable, viscosimetry is impossible.

Table 8
Mass loss during burnout (500 °C) of granules after a treatment with ethanol (boiling under reflux, filtration, drying at 80 °C under vacuum)

Granules	Organics	Mass loss (%)
4	C_{18}-silane	3.74
5	Stearic acid	0.66

5. Conclusion

Silanisation of Si_3N_4 powder surfaces is an effective way to reduce powder–powder interactions. Long chain alkyl silanes provide the strongest effect. As a result, green density is increased significantly. But silanes make a poorer contribution to the reduction of powder–wall interaction—an important prerequisite for good-quality green bodies. For this reason, silanes alone cannot displace classical lubricants as stearic acid can do. As a further additive, however, they allow the preparation of granules which can be compacted to an unusually high green density. More important, compared to usual batches, a certain green density can be achieved by a lower pressure. A simpler technology is possible. Furthermore, the negative effect of overpressing, which is accompanied by macroscopic defects in the green compacts, could be avoided. As a conclusion the optimal way for pressing compacts with high densities and low density gradients is to use the silanisation process in combination with the addition of lubricants. Up to now the results can be applied only for the compaction of Si_3N_4-powders. The examination of transferability to other non-oxid powders should be interesting.

Acknowledgements

This work is supported by the DFG (Deutsche Forschungs-gemeinschaft). Thanks are due to G. Kunz (Cottbus) and B. Schöne (Dresden) for experimental support.

References

1. Doyle, C. A. and Dorsey, J. G., Reversed-phase HPLC: Preparation and characterisation of reversed-phase stationary phases. In *Handbook of HPLC*, ed. E. Katz, R. Eksteen, P. Schoenmakers and N. Miller. Marcel Dekker, New York, 1998, pp. 293–324.
2. Meyer, V. R., *Practical High Performance Liquid Chromatography*. J. Wiley and Sons, Chichester, 1999 pp. 106–110.
3. Busca, G., Lorenzelli, V., Procile, G., Baraton, M. I., Quintard, P. and Marchand, R., FT-IR Study of the surface properties of silicon nitride. *Mater. Chem. Phys.*, 1986, **14**, 123–140.
4. Richter, H. J. and Breuning, U., Surface modification and processing of silicon nitride. In *Proceedings of the 5th European Conference on Advanced Materials and Processes and Applications, Vol. 2, Polymers and Ceramics*, ed. L. A. J. L. Sarton and H. B. Zeedijk. Netherlands Society for Materials Science, Zwijndrecht, 1997, pp. 277–280.
5. Yanez, J. A., Baretzky, B., Wagner, M. and Sigmund, W. M., The adsorption of a tri alkoxy silane on silicon nitride for colloidal processing. *J. Eur. Ceram. Soc.*, 1998, **18**, 1493–1502.
6. Buchta, M. A. and Shih, W. H., Improved aqueous dispersion of silicon nitride with aminosilanes. *J. Am. Ceram. Soc.*, 1996, **79**, 2940–2946.
7. Venkatachari, K. R. and Mutsuddy, B. C., Dispersion of silicon nitride powders in aqueous media with coupling reagents. *Ceram. Trans.*, 1991, **19**, 75–82.
8. Edirisinghe, J., The use of silane coupling agents in ceramic injection moulding: effect on polymer removal. *J. Mater. Sci. Lett.*, 1990, **9**, 1039–1041.
9. Vieth, S., Mitzner, E., Finke, B. and Linke, D., Green bodies from modified silicon nitride powders, part I: powders of different polarity. *Cfi/Ber. DKG*, 2000, **77**(10), E63–E66.
10. Vieth, S., Zeipert-Böckle, S. and Linke, D., Green bodies from modified silicon nitride powders, Part II: Hydrophobic green bodies. *Cfi/Ber. DKG*, 2000, **77**(11-12), E38–E41.
11. Klemm, U., Sobek, D., Schöne, B. and Stockmann, J., Friction measurements during dry compaction of silicone carbide. *J. Eur. Ceram. Soc.*, 1997, **17**, 141–145.
12. Klemm, U. and Sobek, D., Influence of admixing of lubricants on compressibility and compactibility of uranium dioxide powders. *Powder Technology*, 1989, **57**, 135–142.
13. Klemm, U., Sobek, D. and Schöne, B., Möglichkeiten und Grenzen des Einsatzes instrumentierter Preßwerkzeuge bei der Entwicklung und Beurteilung von Preßgranulaten. *Fortschrittsberichte der DKG*, 1996, **11**(1), 103–113.
14. Rabe, T. and Linke, D., Attrition milling of silicon nitride powder under conditions for minimal impurity pickup. *Ceramics International*, 1992, **18**, 161–166.
15. Winter, K., Untersuchungen zur Granulatherstellung in einer Planetenkugelmühle. *Silikattechnik*, 1985, **36**, 1974–1989.
16. Thompson, R. A., Mechanics of powder pressing: model for powder densification. *Am. Ceram. Soc. Bull.*, 1981, **60**, 237–243.
17. Sobek, D., Himpel, G., Klemm, U. and Rabe, T., Methode zur Bestimmung der 3D-Dichteverteilung in Preßkörpern. *Keramische Zeitschrift*, 2001, **53**(3), 198–201.
18. Dörfler, H.-D., *Grenzflächen- und Kolloidchemie*. Verlag Chemie, Weinheim, 1994 pp. 338–345..
19. Myers, D., *Surfaces, interfaces and colloids*. Verlag Chemie, Weinheim, 1991 pp. 214–220, 393–397.