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The influence of lubricants on uniaxial dry pressing of silanised silicon nitride powder

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Abstract

The influence of three surfactants (stearic acid, octadecylamine and octadecyl-trimethoxysilane) on the dry-pressing behaviour of silicon nitride powders was investigated with an instrumented compacting tool. The study reveals that friction processes have a large impact on the compaction behaviour as well as on the properties of green bodies (density, strength, gradients, macroscopic defects). All surfactants reduce friction by boundary lubrication. However, the functional groups cause different interactions of the surfactant molecule with the powder surface, and therefore, different lubrication properties. Octadecyl-trimethoxysilane can form a stable, covalent bond to the powder surface. Hence, it effectively reduces powder–powder friction, but is of little influence on powder–wall friction. This surfactant causes a significant increase of the green density but has only a limited effect on axial density gradients and strength of the green bodies. Stearic acid and octadecylamine have functional groups, which cause only adsorption processes. Therefore, such compounds exhibit an opposite lubrication behaviour with a high efficacy on the die wall. For silicon nitride, stearic acid is more effective than the octadecylamine due to a stronger adsorption of the amine to the silica-like powder surface.

Keywords: Si_3N_4 powders; Surfactants; Lubricants; Pressing; Instrumented press

1. Introduction

Uniaxial dry pressing is an inexpensive forming process of increasing importance.[1] On the other hand, there is a lack in systematic knowledge about the role of the organic additives, necessary for powder compaction.[2] In this paper, the interactions between these additives on the one hand and the surface of the ceramic powder on the other are investigated during the compaction process with an instrumented compacting tool. With such a device a dynamic in situ measurement of relevant processes during compaction, unloading and ejection is possible.[3–5]

Recently, the possibilities of influencing the compaction behaviour of silicon nitride by means of a silanisation of the powder surfaces were described.[6] It appeared to be of interest to continue these experimental studies with a special focus on the active friction processes and, considering the problems caused by density gradients in the green bodies and the wear of the die, the possibilities of lowering pressure gradients in the axial and radial directions.

Therefore, a number of organic additives were chosen, from which a different influence on the friction processes could be expected. Based on our former results it was decided to consider a characteristic surface modifier, octadecyl-trimethoxysilane (OTS),[6,7] and on the other side, stearic acid and octadecylamine, known as typical surface-active compounds which can be used as deflocculants for non-aqueous ceramic slips or as lubricants in ceramic batches for dry

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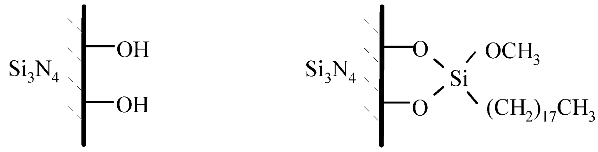

Fig. 1. Silicon nitride powders investigated.

pressing. Both of them have a very similar geometry and differ only in the acid–base behaviour of the functional group.

Silicon nitride was used as the ceramic powder. As shown by different authors,[8] silicon nitride powder has hydroxyl groups at the surface which makes the surface properties very similar to those of silica.

The compaction experiments involved the measurement of wall and powder friction coefficients, ejection forces, force transmission quotients and, derived from these, stress and density gradients. Besides those pressure–density-graphs, measurements of the strength of green bodies, calculations of the compaction energies and a view on the conditions for elastic relaxation contribute to the assessment of the effects of powder silanisation and lubrication.

2. Materials and methods

The reference batches **1** are obtained by milling silicon nitride powder in ethanol. Binder and lubricant were added at the end of the milling procedure, as done in former experiments.[9,10]

Batches **2** are obtained, if silicon nitride powder (UBE SN-E10) was attrition milled[11] in heptane in the presence of octadecyl-trimethoxysilane (OTS) and pyridine[9,10] (Fig. 1, see also Fig. 6). The silane amount was, comparable to former experiments, 0.12 mmol/g. At the end of the appropriate milling procedure the binder polypropylenglycol (PPG 425, amount: of 5 wt.%, related to silicon nitride) and the relevant lubricant (Table 1) were added (1 wt.%). After removal of the solvent, all batches were granulated by rolling granulation, using a planetary mill.[12]

Viscosity measurements were performed on a rotation viscosimeter RHEOTEST 2 (cylindrical set up, Fa. RHEOTEST, Medingen). The compaction behaviour was investigated in an instrumented compacting tool, which allows in situ measurements and calculations of a set of characteristic pressing parameters.[3–5] Primary measured parameters are the forces at the top (F_1) and 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, as necessary for friction experiments. The specially instrumented die insert was made of hardened steel.

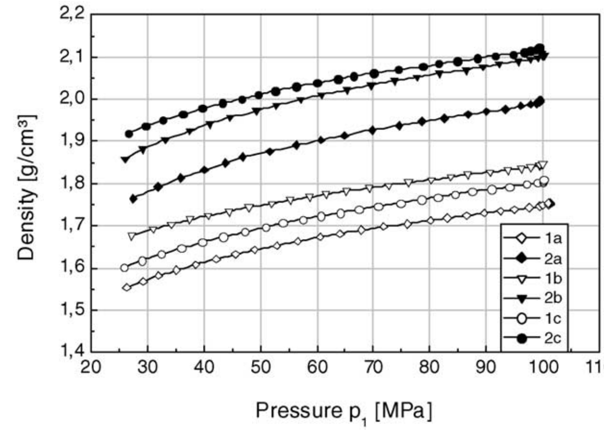

Fig. 2. Dependence of the dynamic measured green density on the pressure for different treated powders.

3. Results

3.1. Compressibility

It is well known, that lubricants usually lead to an increase in the green density. This effect can be observed in a distinct manner for all examined types (see Table 1).

However, the most important result with respect to the compressibility is the change of the powder properties caused by the silanisation (see also Fig. 2). It can clearly be noticed, that the influence of a powder silanisation alone (granules **2a**) predominates over the addition of stearic acid or octadecylamine to common silicon nitride powder (granules **1b** and **1c**) in each case. In the same way a combination of silanisation and lubrication creates possibilities for reaching even higher densities or a drastic reduction of the pressure needed for a specified density (granules **2b** and **2c**). A discussion of the causing mechanisms takes place in Section 4.2.

3.2. Friction conditions

An, as far as possible, even distribution of the applied pressure in axial and radial directions is an important prerequisite

Table 1
Green densities (g/cm^3)

Silicon nitride				Silanised silicon nitride			
Granules no.	Lubricant	At pressure	After unloading	Granules no.	Lubricant	At pressure	After unloading
1a	–	1.76	1.70	**2a**	–	2.00	1.90
1b	Stearic acid	1.85	1.75	**2b**	Stearic acid	2.10	2.00
1c	Octadecyl-amine	1.81	1.72	**2c**	Octadecyl-amine	2.12	2.02

Table 2
Friction related parameters

Silicon nitride						Silanised silicon nitride					
Granules no.	F_2/F_1 (%)	σ_R (MPa)	μ_w	μ_P	F_E (kN)	Granules no.	F_2/F_1 (%)	σ_R (MPa)	μ_w	μ_P	F_E (kN)
1a	49.9	33.5	0.364	0.413	2.26	**2a**	51.8	38.1	0.331	0.322	1.70
1b	72.7	38.3	0.166	0.418	1.25	**2b**	73.1	47.6	0.155	0.296	0.81
1c	73.5	38.5	0.168	0.419	0.85	**2c**	67.4	45.2	0.199	0.302	0.74

F_2/F_1: force transmission coefficient (F_1: top-punch force; F_2: bottom-punch force); σ_R: radial stress; μ_P: friction coefficient (powder–powder); μ_w: friction coefficient (powder–wall); F_E: ejection force.

for green bodies with limited density gradients and a corresponding even shrinkage in the sintering process. This can be reached by reduction of the friction losses between the powder particles and the die wall and between the particles themselves. A better surface quality of the green bodies and a reduced die wear are results of a minimized friction, too. All parameters essential to an assessment of the efficacy of the examined organic additives are summarized in Table 2.

From Fig. 3, representing the dependence of the wall friction coefficients on the pressure, different mechanisms for the reduction of friction can be derived for the individual surfactants. All additives reduce the wall friction coefficient compared to the granules free of lubricant (**1a**). However, the treatment of the silicon nitride powder with octadecyltrimethoxysilane has only a very limited influence on the wall friction coefficient as is shown by a comparison of granules **1a** and **2a**. Only the incorporation of a typical lubricant improves the friction conditions (**1b**,**c** and **2b**,**c**).

A lot of other potential lubricants was examined in the extended study, but for instance neither octylamine nor bis-hydroxyethyl-stearic-acid-amide reached with μ_w between 0.21 and 0.24 the effectiveness of the simple stearic acid.

Basically, all parameters of the compaction process as well as the properties of the green bodies depend on the friction conditions during the compaction of the ceramic batch. One of the most important parameters is the axial force transmission quotient F_2/F_1 (Table 2) which is related to density and stress gradients within the green body.[13] The powder wall friction has the strongest influence on F_2/F_1. Small values of the corresponding coefficient μ_w correlate with a good force transmission (and vice versa). Hence, only batches with a lubricant, particularly stearic acid, can provide high F_2/F_1 values (over 70% for a length/diameter-ratio of the green body of 1:1), regardingless the silanisation.

The ejection force F_E, which is a measure for the static friction of the green body at the die wall, is an important index for the ability of organic additives to found a strong durable layer of lubricant at the die wall. In contrast to the wall friction coefficient an influence of the silanisation on these forces cannot be neglected (Table 2), due to a reduced radial stress in compacts from **2a** to **2c** after unloading (see below).

Fig. 4 the dynamic course of the powder friction coefficients μ_P for selected granules is presented as a function of the pressure. A first remark must concern the role of a lubricant alone for non-silanised granules. Regardless the lower compaction regions, only insignificant differences in the powder friction can be observed between the granules **1a** and **1b** at the specified end pressure. This means, that common lubricants have hardly a potential for decreasing this friction part. On the other hand all silanised types **2a–c** show very low powder friction losses during the compaction. The low μ_P values of **2b** and **2c** cause high values for the radial stress σ_R, thus reducing radial density gradients.

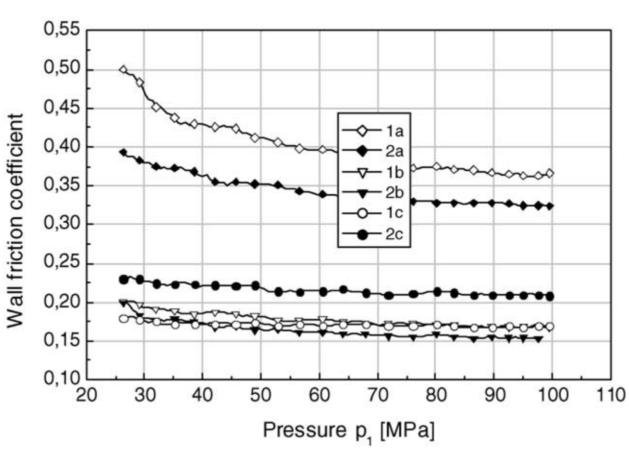

Fig. 3. Dependence of the wall friction coefficient on the pressure for different organics.

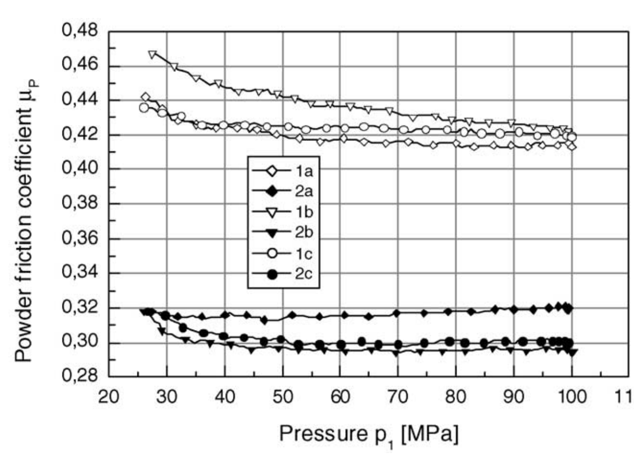

Fig. 4. Dependence of the powder friction coefficient on the pressure for different organics.

Table 3
Elastic relaxation

Silicon nitride			Silanised silicon nitride		
Granules no.	b/l (%)	b_i/b (%)	Granules no.	b/l (%)	b_i/b (%)
1a	2.5	47.6	**2a**	4.2	67.4
1b	2.8	86.0	**2b**	4.2	87.8
1c	4.0	81.8	**2c**	4.2	86.0

l: length of green body; b: total axial relaxation; b_i: part of relaxation inside the die.

According to these results it can be concluded that:

- The wall friction coefficient is above all influenced by conventional lubricants such as stearic acid; a silanisation of the powders results in small changes only.
- The powder friction coefficient can be drastically changed by the silanisation; lubricants are of minor importance.

3.3. Elastic relaxation

In the stage after the maximum pressure, at unloading, an elastic relaxation of the green body takes place (sometimes called spring-back also). It is well-known, that the conditions of the relaxation are responsible for the development of macroscopic pressing defects such as cracks, laminations or end-capping.[3–5] In the same way it is proved, that not so much the absolute amount, but more the place, where this relaxation happens, is important for these processes. If the elastic stresses in the green body can already be reduced to a high degree under controlled conditions inside the die, the danger of defects will be lower.

From the results of Table 3 it can be noticed that an addition of lubricants like stearic acid or octadecylamine is an absolute necessity to reach such desired high values for b_i/b (the so-called "inner parts" of the relaxation). An influence of the silanisation alone is visible but not in an extent sufficient for a clear tear off of the green body from the die wall (Fig. 5). After unloading a higher residual force on the lower punch as a result of higher remaining radial stresses can also be seen, causing larger ejection forces (**1a** and **2a**). Granules with stearic acid show a sharp bend during unloading and very low residual forces (**1b** and **2b**).

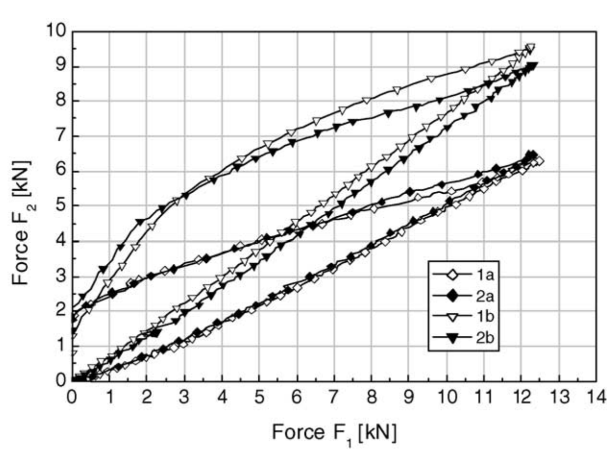

Fig. 5. Loading–unloading curves for granules with different lubrications. Residual forces: (**1a**) 1.83 kN; (**2a**) 1.63 kN; (**1b**) 1.16 kN; (**2b**) 1.45 kN.

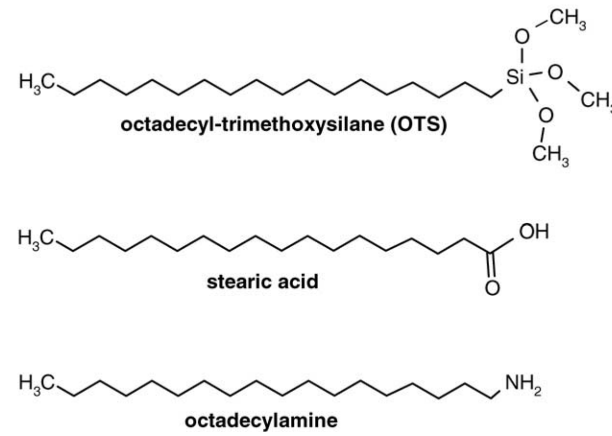

Fig. 6. Structures of octadecyl-trimethoxysilane, stearic acid and octadecylamine.

It attracts attention that for the compaction of all silanised granules higher amounts of the total elastic redeformation were measured. It seems to be clear that the reason is the higher degree of compaction which was obtained with these granules. In the last region of the pressure–density course the part of elastic deformation increases, naturally followed by a higher relaxation.

4. Discussion

4.1. General remarks

Octadecyl-trimethoxysilane, stearic acid and octadecylamine have a very similar molecular geometry (Fig. 6). Each molecule contains a long alkyl chain of 17 or 18 carbon atoms and a small functional group. Thus, all three compounds act as surfactants and show a behaviour, which is known as boundary lubrication or named in rheology as steric stabilisation.[14]

Due to different functionalities, they exhibit a different efficacy regarding powder–powder- and powder–wall-lubrication. The effects of lubricant, silane and binder on μ_P and μ_W can be explained if a powder surface similar to that of silica is assumed[8,15,16] and if the following processes are taken into account:

- adsorption or binding to the powder surface,
- desorption,
- transport processes (in particular from the powder surface to the die wall),
- a reduction of friction mainly by boundary lubrication.

4.2. On the difference between stearic acid and OTS

The results of all experiments show, that stearic acid reduces the powder–wall friction effectively. Already a small

Table 4
Comparison of stearic acid and OTS

Granules no.	Surfactant (mmol/g)			μ_W	μ_P
	Total	Stearic acid	OTS		
1a	–	–	–	0.364	0.413
1b	0.035	0.035	–	0.166	0.418
1m	0.120	0.120	–	0.144	0.394
1l	0.155	0.155	–	0.121	0.379
2a	0.120	–	0.120	0.331	0.322
2m	0.095	0.035	0.060	0.154	0.334
2b	0.155	0.035	0.120	0.155	0.296

μ_P: powder friction coefficient; μ_W: wall friction coefficient.

amount (e.g. 1%, corresponds to 0.035 mmol/g) is sufficient (granules **1b** in Table 4, see also Table 2). A further addition of stearic acid still causes a slight decrease of μ_W (additionally examined granules **1m** and **1l** in Table 4), but would be irrational from a practical point of view. Furthermore, the effect of this surfactant on the powder friction is generally poor. Even large amounts result in only slight improvements. The other surfactant, OTS, exhibits an opposite behaviour. The reduction of μ_W is inefficient, but μ_P is diminished tremendously. This effect can best be seen at granules **1m** and **2a**, which have equal molar amounts of stearic acid respective OTS as the only surfactant. Also the pairs **1l**/**2b** and **1m**/**2m** are instructive. Granules, which contain both surfactants, exhibit both low μ_P and μ_W values (**2b**/**2h)**. Regarding powder friction, better results were obtained (**2b**) when the surface was fully covered by the silane.[9,10]

A significant reduction of the powder–wall friction can only be achieved, if the lubricant has a sufficient mobility from the powder-surface to the wall.[3–5] In Fig. 7 the course of the force transmission coefficient dependent on the pressure is recorded.

The compaction of granules with stearic acid results in a high, nearly constant quotient (**1b** and **2b**) during the entire process, because stearic acid is present at the wall from the beginning of the compaction process. In contrast, it can be seen that the compaction of granules with added OTS (**2a**) only leads to a low F_2/F_1 and, which is more important, an increase of the quotient with growing pressure. This behaviour is always observed, if no effective lubricant is present.[3–5] **1a** yields a very similar curve. Stick-slip mechanisms at the wall, in particular in the low-pressure region, seem to be the reason for the slope. This underlines again, that the alkylsilyl groups are bound in a very stable manner to the powder surface and cannot contribute to an effective reduction of the powder–wall friction.

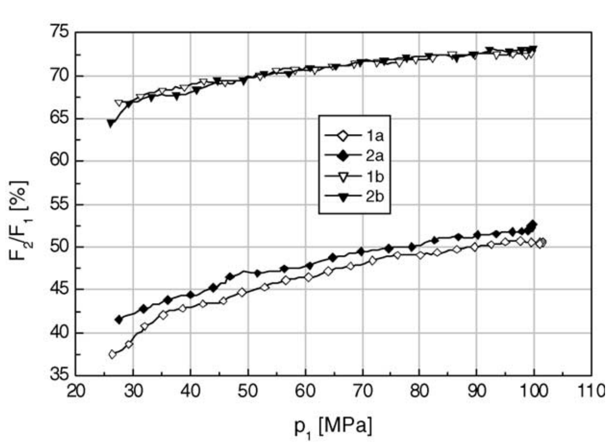

Fig. 7. Dependence of the axial force transmission on the pressure.

Regarding the reduction of powder–powder friction, a stable bond between surfactant and powder surface is necessary. Thus, the surfactant is not removed by the strong shearing forces during the compaction process. As shown in previous studies,[6,7] the silane has the strongest effect, due to the fixation by a covalent bond. Stearic acid as a typical wall lubricant causes a smaller μ_P reduction. Hence, a weak bond—an advantage for wall lubrication—is a disadvantage in powder–powder lubrication. However, stearic acid causes a further reduction of the μ_P of silanised granules (compare **2a** and **2b** in Table 4). Obviously, the acid binds to non-silanised areas of the surface, the so-called “hot spots”,[17–19] thus improving the boundary lubrication.

As shown, the green density correlates with μ_P.[6,7] Pressure–density functions in Fig. 2 confirm this result. Furthermore, the reduction of μ_P changes the effect of loads. Whereas non-silanised powders transfer loads throughout compact mainly in the direction of application (e.g. **1b**) large portions of the load act also in the perpendicular direction if silanised powders are used (e.g. **2b**). As a result, **2b** exhibits a high radial tension σ_R at the end of the compaction process (see Table 2), which reduces density gradients in the radial direction. It has to be mentioned that after removal of load and punches relaxation is easier for **2b** (compared to **1b**). This has two consequences. First, **2b** shows higher values for the spring back inside the die (both total and relative), which is combined with a lower σ_R value at that stage (**1b**: 6.9 MPa; **2b**: 3.4 MPa). By this reason, ejection of the compact is easier (compare F_E in Table 2).

Stearic acid and OTS have also an opposite effect on green strength (Table 5). The lubricant diminishes friction losses (in

Table 5
Energy parameters and green strength

Granules no.	W_F (Nm)	W_U (Nm)	σ_{DC} (MPa)	Granules no.	W_F (Nm)	W_U (Nm)	σ_{DC} (MPa)
1a	10.1	5.9	0.53	**2a**	10.1	6.6	0.34
1b	5.8	11.1	0.78	**2b**	5.2	9.4	0.54

W_F: friction energy; W_U: energy uptake; σ_D: diametral compressive strength (at a pressure of 100 MPa).

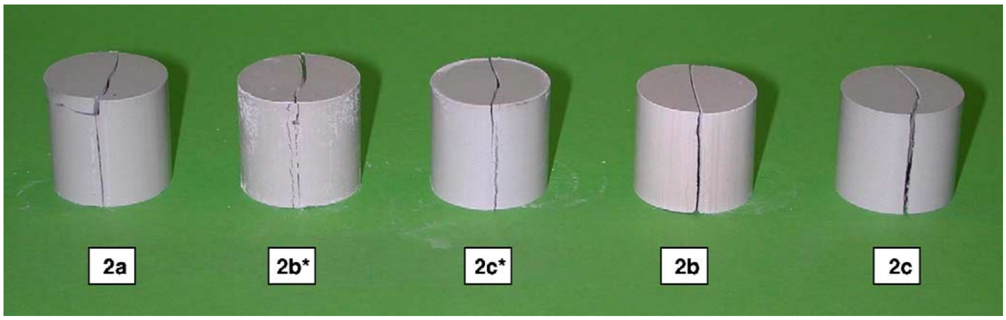

Fig. 8. Fracture pictures of green bodies after measurements of diametral compressive strength (samples marked with a "*" are prepared from binder-free batches).

particular at the die wall) thus increasing the energy uptake W_U, a measure which is strongly related to strength.[3–5,20]

OTS is reducing powder–powder interactions. Therefore, also strength is slightly reduced. Despite the lowered strength, compacts from granules **2b** and **c** caused no problems while handled and showed no signs of macroscopic defects during the measurements of diametral compressive strength and in the resulting fracture pictures (Fig. 8). The further examples shown in Fig. 8 underline the necessity of both binder and lubricant in ceramic batches. Otherwise the fracture pictures indicate remarkable defects.

4.3. *On the difference between stearic acid and octadecylamine*

The lubrication behaviour of octadecylamine and stearic acid is of the same kind. Both compounds reduce significantly μ_W, but the effect on μ_P is rather poor. However, there are small, but significant differences between the two organics. It is known from silicon nitride[21,22] as well as from silica,[17,18] that amines are more strongly adsorbed by the powder surface than acids, due to the weakly acidic character of the surface. This effect is also found in silanised silicas[17–19] and is confirmed for silanised silicon nitride by the results presented in Fig. 9. The amine causes smaller shear stresses than the acid. This slightly stronger fixation is a disadvantage for transport processes. Therefore, compared to stearic acid, an addition of octadecylamine leads to higher μ_W values in all cases (Table 2).

Considering the discussion about the binding strength, it should be expected that octadecylamine reduces μ_P more effectively than stearic acid, which is not observed. Obviously, the fixation of the amine is still too weak (compared to OTS) and therefore, shows no relevance to the compaction process.

4.4. *Influence of the binder*

This work focuses on the effect of surfactants. By this reason, for all batches amount and type of the binder were identical (polypropylenglycol, PPG 425). For comparison also granules without binder are prepared. The results (not shown in detail) indicate that the binder itself has only poor lubrication properties and also cannot significantly alter the effect of the surfactants investigated. On the other hand an organic binder is a necessary additive regarding the quality of green bodies, because it compensates the high inner stresses in the compacts. Without binder, in nearly all cases irregular fracture pictures arise after the measurement of the diametral compressive strength, which points to serious macroscopic failures (compare Fig. 8).

The influence of binder variations on the compaction behaviour and on green-body properties is a topic for further research.

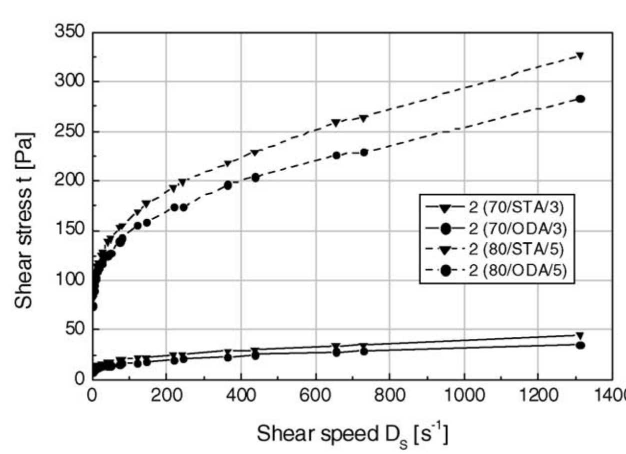

Fig. 9. Flow curves of the silanised powder, suspended in *n*-heptane (powder content/lubricant type/lubricant content; STA: stearic acid; ODA: octadecylamine).

5. Conclusions

An extended study was carried out with respect to the influence of different surfactants on the lubrication conditions at uniaxial dry pressing, because friction processes have a large impact on the compaction behaviour of granules as well as on the properties of green bodies. A set of typical parameters, suitable for characterising the pressing process as a whole, was measured with an instrumented compacting tool.

Surfactants cause boundary lubrication. The efficacy on powder–wall or powder–powder friction depends on the functional group of the surfactant. A group which can form a stable, in particular covalent, bond to the powder surface leads to a surfactant, which effectively reduces powder–powder friction, but is of little influence on powder–wall friction. Such a surfactant causes a significant increase of the green density for a given pressure, but has only a little effect on axial density gradients and strength in the green bodies. It was as established, that especially silanes show such behaviour.

On the other hand, typical lubricants, such as stearic acid and octadecylamine have functional groups, which only cause adsorption processes. The fixation is weaker. Hence, such organics exhibit an opposite lubrication behaviour. They improve all parameters, which depend on good powder–wall lubrication, resulting in reduced density gradients, but they are of little influence regarding green density. For silicon nitride the acidic lubricant is more effective than the basic one.

From the practical point of view, granules should obtain both strong and weak bounded surfactants, e.g. OTS and stearic acid. This combination allows the compaction of granules to green bodies with a high green density, small density gradients and a sufficient strength.

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References

1. Bartusch, R., Preßgranulate “nach Maß” durch Sprühtrocknung. *Keramische Zeitschrift*, 2000, **52**(9), 758–765.
2. Reh, H., An der Wiege der modernen Keramik. *Cfi/Ber. DKG*, 1999, **76**(11/12), D33–D36.
3. 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.
4. Klemm, U. and Sobek, D., Influence of admixing of lubricants on compressibility and compactibility of uranium dioxide powders. *Powder Technol.*, 1989, **57**, 135–142.
5. 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.
6. Vieth, S., Uhlmann, M., Linke, D., Klemm, U., Sobek, D. and Börner, F.-D., Effect of surface silanisation on the dry pressing behaviour of silicon nitride powder. *J. Eur. Ceram. Soc.*, 2003, **12**, 1997–2004.
7. Vieth, S., Linke, D., Klemm, U. and Sobek D., In-situ investigation of the compaction of surface-modified silicon nitride powders (poster). In *Conference and exhibition of the European Ceramic Society*, Brügge, September 9–13, 2001. *Key Eng. Mater.*, 2002, **206**–**213**, 103–106.
8. (a) 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;
(b) Schmidt, H. and Ziegler, G., *Analysis and Surface Chemistry of Silicon Nitried Powders: THIRD EURO-CERAMICS*. Faenza Editrice Iberica S.L, 1993;
(c) Danforth, S. C., Symons, W., Nilsen, K. J. and Riman, R. E., In J. G. P. Binner (Ed.), *Advanced Ceramic Processing* (*Vol 1*), 1992. 4953 pp.
9. Vieth, S., Mitzner, E., Finke, E. 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. Rabe, T. and Linke, D., Attrition milling of silicon nitride powder under conditions for minimal impurity pickup. *Ceram. Int.*, 1992, **18**, 161–166.
12. Winter, K., Untersuchungen zur Granulatherstellung in einer Planetenkugelmühle. *Silikattechnik*, 1985, **36**, 1974–1989.
13. Sobek, D., Himpel, G., Klemm, U. and Rabe, T., Methode zur Bestimmung der 3D-Dichteverteilung in Preßkörpern. *Keramische Zeitschrift*, 2001, **53**(3), 198–201.
14. (a) Dörfler, H.-D., *Grenzflächen- und Kolloidchemie*. Verlag Chemie, Weinheim, 1994;
(b) Myers, D., *Surfaces, Interfaces and Colloids*. Verlag Chemie, Weinheim, 1991.
15. Schmidt, H. and Ziegler, H., Analysis and surface chemistry of silicon nitried powders. In *THIRD EURO-CERAMICS*, ed. P. Durán and J. F. Fernandez. Faenza Editrice Iberica S.L, 1993, pp. 137–142.
16. Danforth, S. C., Symons, W., Nilsen, K. J. and Riman, R. E., *Advanced Ceramic Processing*(*Vol 1*), ed. J. G. P. Binner. 4953 pp.
17. 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.
18. Meyer, V. R., *Practical High Performance Liquid Chromatography*. John Wiley and Sons, Chichester, 1999.
19. Vieth, S., Mitzner, E. and Linke, D., Indirect characterisations of modified silicon nitride powders by chromatography. In *Euromat, München 1999. Vol 12: Ceramics, Processing, Reliability, Tribology and Wear*. Wiley-VCH, Weinheim, 2000, pp. 134–138.
20. Klemm, U., Sobek, D., Schöne, B., Vieth, S. and Linke, D., Instrumentierte Pressverdichtung und Formkörpereigenschaften. In *DKG Technische Keramische Werkstoffe*, ed. J. Kriegsmann. Verlag Deutscher Wirtschaftsdienst, 2002, Kap. 3.4.3.4.
21. Bergström, L. and Liden, E., Effects of surface modification on the adsorption behaviour and dispersion of silicon nitride powders in non-aqueous media. *Ceram. Trans.*, 1991, **22**, 289–295, Ceramic Powder Science IV.
22. Wang, L., Sigmund, W. and Aldinger, F., Kolloid-Pulverprocessing von nichtoxidkeramischen Massen(Si_3N_4). In *DKG Technische Keramische Werkstoffe*, ed. J. Kriegesmann. Verlag Deutscher Wirtschaftsdienst, Köln, 2001, Kap. 3.3.3.2.