Ceramics International 22 (1996) 113-117

0272-8842/96/$15.00
0272-8842(95)00065-8

Mechanical Properties of Green Compacts with Coated Powders

Chong-Min. Wang

Department of Materials Science, Lanzhou University, Lanzhou, Gans, People's Republic of China

(Received 24 March 1994; accepted 1 March 1995)

Abstract: The mechanical properties of green compacts in the coated powders system of silicon nitride coated with alumina have been systematically investigated from the point of view of bend strength, strength distribution, green compact formation pressure and densities. More generally, factors contributing to the commonly observed significantly high green compact strength with coated powders are considered on the basis of the microstructural behaviour of the coating layer nano-dimension particles and the particle contact mechanics.

1 INTRODUCTION

A new development in the processing of engineering ceramics is termed 'powder coating'.[1-4] Powder coating can be accomplished by sol–gel and *in-situ* solution precipitation processes. The benefit of powder coating can be seen in general, as expected, in the homogeneous distribution of the sintering additive on particle size scale, fast densification and improvement of homogeneity of the sintered materials.[1,2] Apart from these, another distinctive feature for coated powders is the reported high green compact strength as for example ZrO_2-coated Al_2O_3, ~15 MPa, and Si_3N_4 coated with Mg–Al oxide, ~27 MPa.[2] From the industrial point of view, it is of great importance to obtain high green compact strength, and hence a systematic characterisation of the green compact strength in using coated powder is desirable. In this study, the mechanical properties of Si_3N_4 powder coated with Al_2O_3 by the *in-situ* precipitation process are systematically investigated in terms of green compact strength, Weibull modulus, and coated powder particle morphology change upon compacting.

2 EXPERIMENTAL

Silicon nitride powder (Si_3N_4) (LC12N, H. C. Starck, Germany) is coated with different levels of Al_2O_3 by the following process. Aluminium *iso*-propoxide ($Al[OCH(CH_3)_2]_3$) (BDH Chemicals, Poole, UK) is dissolved in *iso*-propanol with a concentration of aluminium-*iso*-propoxide: *iso*-propanol of 1:20 g cm^{-3}, and the Si_3N_4 powder added to the solution. In order to improve the dispersion of the Si_3N_4 powder, and the alkoxide adsorption on Si_3N_4 particle surfaces, the slurry is ball milled for 24 h and then transferred to a flask under flowing nitrogen for controlled hydrolysis. A molar ratio of the total water to alkoxide of 20:1 is chosen to ensure complete hydrolysis of the alkoxide by deionised water diluted by *iso*-propanol to give a water concentration of 33% (by volume). Water is added to the slurry at 75°C using dropwise addition (3 cm^3 min^{-1}) with vigorous magnetic stirring. On completion of hydrolysis, the slurry is dried under infrared radiation at 50°C and then at 120°C for 2 h to obtain a powder. For comparison purposes, the pure aluminium hydroxide coating phase is obtained by hydrolysis of aluminium *iso*-propoxide under identical conditions without addition of Si_3N_4 powder.

The coated powders are isostatically compacted through a range of pressures from 50 MPa to 400 MPa to obtain green bodies for strength measurements. The strength of the green body is determined by a standard four-point bending test with outer and inner span of 18 mm and 6 mm, as well as by diametral compression.[5] The diametral strength was obtained by compression of a disc on a diameter.

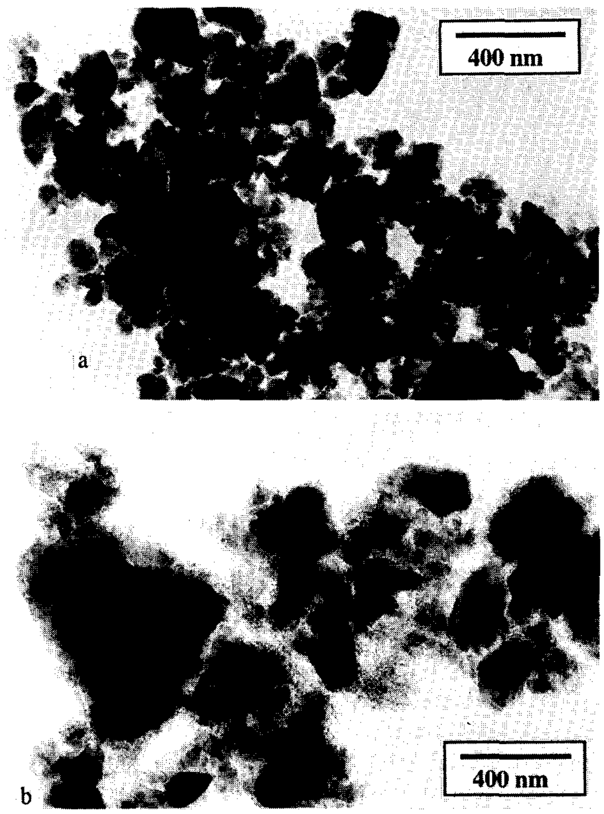

Fig. 1. TEM micrographs of (a) as-received and (b) hydrated aluminium oxide-coated Si_3N_4 powders (15wt% Al_2O_3).

The strength σ_f was calculated according to:

$$\sigma_f = 2P/(\pi DT) \qquad (1)$$

where P is the load at fracture and D and T are the specimen diameter and thickness.

The strength distribution function is calculated according to the two-parameter Weibull function:[6]

$$P_f = 1 - \exp[-(\sigma/\sigma_0)^m] \qquad (2)$$

where σ is the strength, σ_0 is the characteristic strength, P_f is the failure probability, and m is the Weibull modulus. For a group of specimens N, P_f is calculated by the median ranking method,[7]

$$P_f = (i - 0{\cdot}3)/(N + 0{\cdot}4) \qquad (3)$$

The diametral compression green body samples of 8 mm diameter and 3 mm thickness are prepared by uniaxially pressing powder at 50 MPa, and then isostatically pressing the cylinder to the desired pressure in a sealed plastic envelope. Samples of compacted powder for four-point bend strength testing are obtained by direct isostatic pressing of powder in a rubber mould, and then cutting into 30 × 6 × 6 mm^3 bars. Surfaces are ground with 1200 grade silicon carbide paper, and the edge left unbevelled. All strength measurements are carried out using an Instron Universal Testing Machine (Type 115 UK) with a cross-head speed of 0·1 mm min^{-1}. Powder morphology is observed by transmission electron microscopy (TEM) (Jeol-JEM 200CX) with a standard powder doping process on copper grid. In the case of compacted powder, the compacted powders are ground to observe the coating layer change upon pressing.

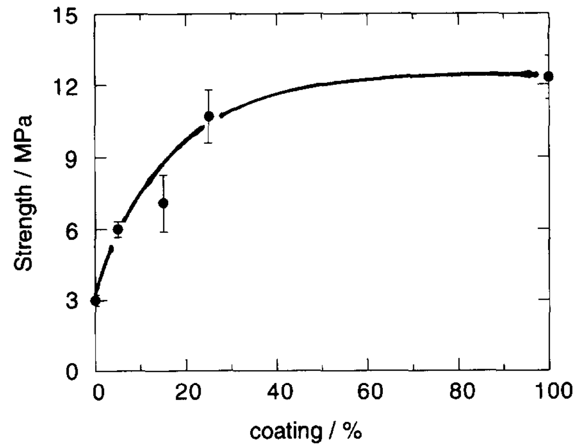

Fig. 2. Four-point bend strength at a constant solid volume fraction, ϕ = 0·62, as a function of coating amount.

3 RESULTS

Figure 1 shows the general morphology of the as-received Si_3N_4 powder and 15wt% Al_2O_3-coated powders. Clearly Si_3N_4 particles with a particle size of ~500 nm are clad by the hydrolysed needle-like aluminium hydrate. Four-point bend strength at a relative density (ϕ) of 0·62 is shown as a function of coating amount in Fig. 2. The strength increases with increasing coating and reaches a plateau, corresponding approximately to the strength of the pure coating phase, at a level of ~25%. The Weibull distribution of diametral strength for different coating levels is shown in Fig. 3. The Weibull modulus has a maximum value at a coating level of 5%. Strength as a function of solid volume fraction, ϕ, for 25% coated powder is shown in

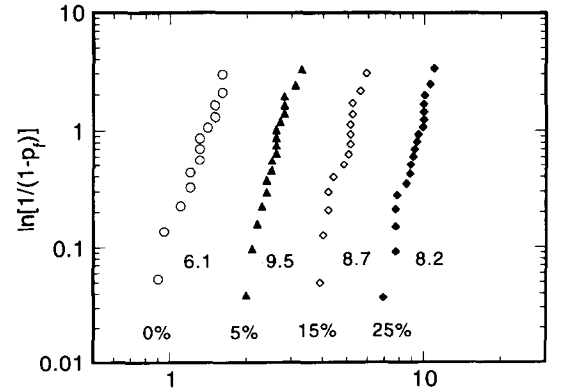

Fig. 3. Weibull distribution of diametral strength of powders with varying amounts of coating at a constant solid volume fraction ϕ = 0·55.

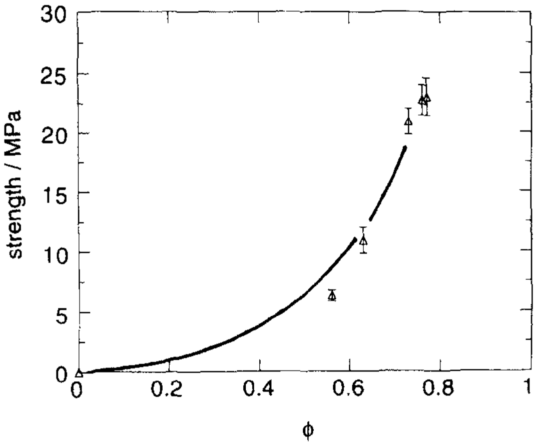

Fig. 4. Four-point bend strength as a function of solid volume fraction, ϕ (25wt% coatings).

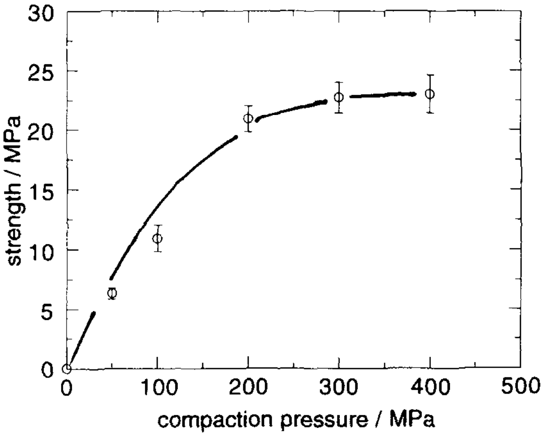

Fig. 5. Four-point bend strength as a function of compaction pressure (25wt% coatings).

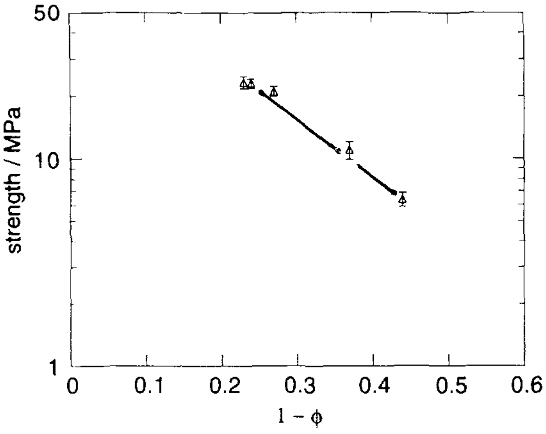

Fig. 6. Four-point bend strength as a function of pore fraction, (1-ϕ)(25wt% coatings).

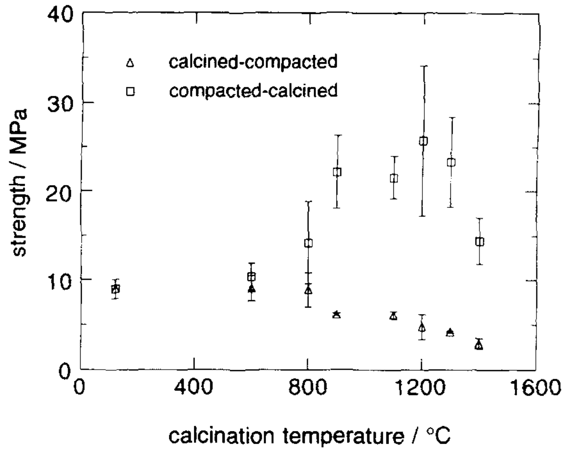

Fig. 7. Diametral strength as a function of calcination temperature (25wt% coatings).

Fig. 4. Figure 5 similarly shows strength as a function of isostatic compaction pressure. Strength increases markedly with increasing compaction pressure within the range 0–200 MPa; above 200 MPa, strength reaches a plateau. The logarithm of strength as a function of pore fraction for 25% coated powder is plotted in Fig. 6, which can be fitted into a straight line with a correlation coefficient 0·99 as:

$$\sigma = 104 \exp(-\,6{\cdot}25\,p) \qquad (4)$$

where σ is strength in MPa, and p is pore fraction.

Diametral strength as a function of calcining temperature is shown in Fig. 7, for which the effect of the sequences of calcining and compaction have been examined. If the powder is compacted and calcined, the strength increases with increasing calcining temperature up to 1300°C, and falls at 1400°C. In reverse, the strength decreases continuously with increasing calcination temperature. The morphological change after compaction at 400 MPa of 15% coated powder is shown in Fig. 8. On compaction, the open structure of the coating layer collapses to a more dense layer.

4 DISCUSSION

The low bulk density nature of the coated particles has been clearly demonstrated by the compaction behaviour of the coated powders.[1] This shows two

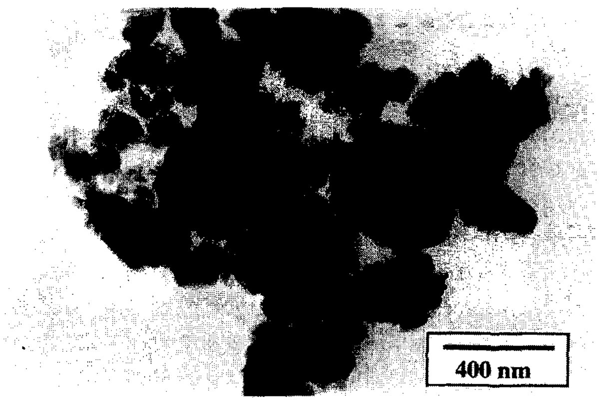

Fig. 8. TEM micrograph of Si_3N_4 particles coated with hydrated aluminium oxide (15% Al_2O_3) and after compacted at 400 MPa showing the coating layer is compressed as compared with Fig. 1.

marked features. The first is the low packing density obtained with low (~10 MPa) compaction pressures. The second is that the compressibility of the coating is very high, and at pressures > 100 MPa, a significantly high packing density can be achieved. With increase of the coating amount up to 25% equivalent Al_2O_3, a relative density of 0·70 can be achieved at a compaction pressure of 200 MPa. Experimental and theoretical considerations show that by mixing small and large spheres with a diameter ratio of 1 : 20 and mixing fraction of 1 : 3, the highest relative density reached is 0·86.[8] A bimodal mixture of 10-nm and 100-nm silica particles has been shown to give a maximum relative density of 0·68 at 30 vol% of fine particles.[9] However, in reality, ceramic particles are not spherical or monosized. It is certain that mixing two graded particle size powders is beneficial for a high green compact density, and an initially homogeneous distribution of the small particles is also desirable.

The fracture mechanism of a green body has been developed by Rumf, based on the various mechanisms of particle adhesion such as van der Waals force, liquid bridges and solid binding.[10] Recently, Kendall has modified the model of Rumf mainly based on the contacted particle surface interaction such as van der Waals attraction.[11-14] It is hence theoretically concluded that the strength of a green compact is proportional to the fourth power of compaction fraction (ϕ) and inversely proportional to the square root of particle size. The aggregate properties of the coating layer may account for the high green compact strength seen with coated powders. For normal ceramic powders, green compact strengths are in the range of ~1–2 MPa.[15] The coated powder green compact strength initially increases with increasing amount of coating and then reaches a plateau value approximately that for the pure coating phase.

From Kendall's study, green compact strength, σ, can be expressed as

$$\sigma = 15{\cdot}6\ \phi^4\ \Gamma(dc)^{-1/2} \qquad (5)$$

where Γ is the particle adhesion energy, d is particle size, c is the defect size, and ϕ is solid volume fraction. As the coating amount increases from zero, two factors become relevant: first, the change of particle adhesion energy from that of pure Si_3N_4 to that of the Si_3N_4-coating layer; secondly, the very fine coating layer particles effectively reduce the particle size of the system. These factors may contribute to the high green compact strengths seen with coated powder. Estimates of compact strength may be made using $\Gamma = 0{\cdot}5$ J m^{-2} (typical of ceramic powders),[16] c as the maximum particle size of Si_3N_4, 500 nm, for pure Si_3N_4 d is 100 nm (from BET), for 25% coated powder d is 10 nm (from BET) and with a solid volume fraction ϕ = 0·62, from eqn (5), the strengths of pure Si_3N_4 and 25% coated Si_3N_4 should be 5 MPa and 16 MPa. This is consistent with the experimental values. With increasing amount of coating, the powder progressively behaves more like a pure coating layer material, and up to a certain extent the powder properties are mainly governed by the coating layer. A saturation coating level of 30% by volume is indicated. In theory, the saturation value could be considered as the Si_3N_4 particles arranged in a hexagonal closest packing with a filling fraction of 74% and the remaining pores filled by coating layer materials.

The mechanical difference between a green body and a sintered one is mainly determined by the fracture energy. For a sintered body, the fracture energy is determined by a variety of factors such as bonding fracture. For a green body it is mainly controlled by the particle interactions on the molecular scale, such as van der Waals forces,[12] and the fracture energy or particle adhesion energy is only 1/30 of that of sintered body (for Si_3N_4, fracture energy is 20–30 J m^{-2}).[17] At this point, the particle adhesion energy becomes the limiting factor for the improvement of green body strength. The maximum green compact strength can be obtained from eqn (4) by extrapolating to zero porosity, and calculated theoretically from eqn (5) with d = 10 nm, c = 500 nm, $\Gamma = 0{\cdot}5$ J m^{-2} and ϕ = 1, which both give a strength of ~100 MPa. This means that the strength of even a green compact with zero fraction of porosity is still far lower than that of a partially sintered body such as reaction-bonded silicon nitride (RBSN).[18]

The transition from particle adhesion in the green state to particle bonding in the sintered or partially sintered body is represented by the calcining process. The effect of calcination on green compact strength is distinguished by the sequence of compaction and calcination. If powder is first calcined and then compacted, the strength decreases with increasing calcining temperature. But in the reverse case, calcination is likely to cause particle bonding and the strength increases with increasing calcination temperature up to 1300°C.

The Weibull modulus is a reflection of the flaw size distribution in a material;[19] the narrower the flaw size distribution, the larger the Weibull modulus. Generally, ceramic green bodies have a Weibull modulus of ~7,[15] as for pure Si_3N_4 in this work, but with powder coating the Weibull modulus becomes 9 for 5% coating. It is clear that the coated powder green compact is more homogeneous than the uncoated one.

5 CONCLUSIONS

Significantly high green compact strength is attainable with coated powders. The strength increases with increasing coating content and reaches a saturation value which approximately corresponds to that of the pure coating materials. The most probable reasons for the high green strengths are the finer particle size of the coating layer material, and the relatively high compaction density, in accordance with Kendall's model. Extrapolated experimentally and estimated theoretically, the maximum green compact strength should be ~100 MPa. These features seem likely to be common to all similarly coated powders.[2,20,21] With compaction and calcination of the green body, the strength increases because of bonding of the aggregated particles. The coating is thus a very effective 'low loss' binder, with minimal loss of material during heating to sintering temperature.

ACKNOWLEDGEMENT

The author is grateful to Dr F. L. Riley at The School of Materials, University of Leeds, UK, for constructive criticisms of the experimental works.

REFERENCES

1. WANG, C. M. & RILEY, F. L., Alumina coating of silicon nitride powders. *J. European Ceram. Soc.*, **10** (1992) 83–93.
2. KULIG, M., OROSCHIN, W. & GREIL, P., Sol–gel coating of silicon nitride with Mg–Al oxide sintering aid. *J. European Ceram. Soc.*, **5** (1989) 209–17.
3. WANG, C. M. & ZHE, X. L., Coating layer formation mechanism in coating of Si_3N_4 particles. *J. Mater. Sci. Lett.*, **14** (1995) 129–31.
4. WANG, C. M. & RILEY, F. L., Morphological changes during the calcination of oxide coated silicon nitride powder. *British Ceram. Proceedings*, **53** (1994) 235–48.
5. WANG, C. M., Processing of coated silicon nitride powders. PhD Thesis, University of Leeds, UK, 1993.
6. WEIBULL, W., *J. Appl. Mech.*, **18** (1951) 293.
7. OVRI, J. E. O. & DAVIES, T. J., Uniaxial and biaxial strength of a sintered ferrite. *Sci. of Ceram.*, **14** (1988) 599–605.
8. FINNEY, J. L., Random packing and the strength of single liquids: I. The geometry of random close packing. *Proc. R. Soc. Ser. A*, **319** (1970) 479–89.
9. GAUTHIER, F. G. R. & DANFORTH, S. C., Packing of bimodel mixtures of colloidal silica. *J. Mater. Sci.*, **26** (1991) 6035–40.
10. RUMF, H., *Chem. Ing. Tech.*, **30** (1958) 144.
11. KENDALL, K., McNALFORD, N. & BIRCHALL, J. D., The strength of green bodies. *Special Ceramics*, **8** (1986) 255–65.
12. KENDALL, K., McNALFORD, N., LEGG, W. J. & BIRCHALL, J. D., Flocculation clustering and weakness of ceramics. *Nature*, **339** (1989) 11–12.
13. KENDALL, K., McNALFORD, N. & BIRCHALL, J. D., *Nature*, **325** (1987) 277.
14. KENDALL, K., Microstructure of submicron powders and green compacts. *British Ceram. Proceedings*, **42** (1989) 81–90.
15. KENDALL, K., McNALFORD, N. & BIRCHALL, J. D., *British Ceram. Proceedings — Special Ceramics*, **37** (1986) 255–65.
16. KENDALL, K., Agglomerate strength. *Powder Metall.*, **31** (1988) 28–31.
17. RICE, R. W., McKINNEY, K. R., WU, C. C. M. & FREIMAN, S. W., *J. Mater. Sci.*, **20** (1985) 1392.
18. RILEY, F. L., Reaction bonded silicon nitride. *Materials Science Forum*, **47** (1989) 70–83.
19. PAMPUCH, R. & HABERKO, K., In *Ceramic Powders*, ed. P. Vincenzini. Plenum Press, New York, 1983, p. 623.
20. STEPHEN, R. G. & RILEY, F. L., Compaction behaviour of oxide silicon powder. *J. European Ceram. Soc.*, **9** (1992) 301–7.
21. WANG, C. M. & RILEY, F. L., Microstructure control in silicon nitride by particle coating. *Key Engineering Materials*, **89-19** (1993) 135–9.