Ceramics International 24 (1998) 99–104

0272-8842/97 $17.00+.00
PII: S0272-8842(96)00085-5

The Effects of Atmosphere on the Thermal Debinding of Injection Moulded Si_3N_4 Components

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(Received 15 July 1996; accepted 19 September 1996)

Abstract: The thermal debinding of injection moulded silicon nitride components under nitrogen, air, and $N_2+5\%H_2$ atmospheres at various temperatures was investigated. The softening points and bonding structure of binders, pore size distribution, density and strength were studied. Results indicated that a slow binder removing rate and control debinding atmosphere are essential to the sintered properties. © 1997 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Ceramic powder injection moulding has attracted much attention in the last decade. Much investigation in this area has concentrated on developing a near-net shape process for manufacturing complex-shaped and low cost components of high performance. The injection moulding techniques has been applied to ceramic materials such as Si_3N_4, Al_2O_3, TiB_2, and ZrO_2.[1–4]

The design of binder system is one important subject in the process of injection moulding.[5–7] The compatibility between binders and ceramic powders greatly affects the rheology of suspension[8] and debinding time. Debinding atmospheres were also known to play an important role during thermal debinding, although their debinding mechanisms were still not well understood.[9–11]

The thermal debinding of injection moulded silicon nitride components under nitrogen, air, and $N_2 + 5\%H_2$ atmospheres at various temperatures were investigated in this paper. The weight loss, porosity, softening points, bonding structure of binders, pore size distribution, density and strength of injection moulded Si_3N_4 components were studied.

2 EXPERIMENTAL PROCEDURE

2.1 Processing

Silicon nitride powder (92 wt%, LC 12, H. C. Stark, Goslar, Germany), average particle size of 0.6 μm was mixed with yttria (6 wt%, 5603, Molycorp, USA), with an average particle size of 1.8 μm and alumina (2 wt%, 16 SG, Alcoa, USA), with an average particle size of 0.5 μm, in a polyurethane bottle with high-purity alumina balls and ethanol for 24 h. The slurry was then dried in a rotating vacuum condenser, ground with an alumina mortar and pestle, and screened through a 100-mesh screen for pulverizing aggregates.

Binders used in this study included polypropylene (PP), paraffin wax (PW), diethyl phthalate (DEP) and stearic acid (SA). Trace of diethyl phthalate was used as plasticizer. A solid loading of 55 vol% silicon nitride (including sintering additives) was used. Blending was conducted in a double-bladed mixer (Irie Shokai Co., Japan, PN-1H) at 215°C with 35–45 rpm.

The barrel temperatures used for injection were 215, 205, and 215°C from feeder to nozzle, respectively. The injection pressure and injection rate were 55.9 MPa and 40 $cm^3 s^{-1}$, respectively. The

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dimensions of the as-injected samples were 95x12x4 mm.

Samples were thermally debinded under different atmospheres (air, nitrogen and $N_2 + 5\%H_2$) after injection moulding. They were then sintered in covering powders made of the same composition in a graphite furnace (Centorr/Vacuum Industries, Inc., Model 10-2) at 1800°C under a nitrogen pressure of 1 atm. for 1 h.

2.2 Analysis

The thermal behaviour of binders was examined by differential scanning calorimetry (DSC). The weight change during debinding was determined by thermogravimetric analysis (TG/DTA, Setaram TAG24) in temperatures ranging from 70 to 600°C. In order to understand the bonding structure of binders during thermal decomposition, an infra-red spectroscopy (IR) analysis was conducted at various temperatures. A mercury porosimeter (Micromeritics Instrument Co., Autopore II 9215, USA) was used to analyse the pore structure.

The density was measured by a water displacement technique. Flexural strength was determined by four-point bending on a universal testing machine (Shimadzu AGS 500D, Japan) at a displacement rate of 0.5 mm mm^{-1}. The outer and inner spans used were 40 mm and 20 mm, respectively. The nominal dimensions of the testing bars were 3x4x45 mm with 45° edge chambers.

3 RESULTS AND DISCUSSION

3.1 Characterization of binders

The DSC and TG analysis were conducted on PP, PW, SA, and DEP separately in air as shown in Figs 1 and 2. The results illustrated the softening points (Fig. 1) and weight loss (Fig. 2) of various binders at different temperatures.

In order to investigate the possible interactions among binders themselves and between binders and ceramics, binders were also mixed with Si_3N_4 powders before conducting DSC analysis, and the results were compared with Fig. 1 (Fig. 3). Results indicated that the softening points of SA and PW overlapped. In addition, the softening points of all binders decreased in comparison with Fig. 1. This was probably due to the interfacial reactions between the ceramic powder and binders, and the increase in plasticity and fluidity resulting from the increase of contact area due to mixing of binders.

In order to investigate the effects of the atmosphere on the softening points of binders, DSC analysis was also conducted in nitrogen gas, and the results were compared with Fig. 3 (Fig. 4). The results revealed that the softening points of SA, PW and PP in air were consistently lower than in N_2. This suggested that the bonding structure and flowability could be different in different atmospheres.[9] This is in agreement with the results from TG analysis that also indicated that the thermal

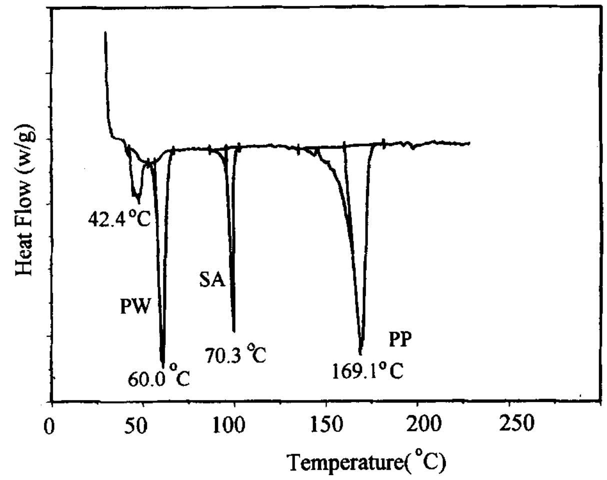

Fig. 1. DSC analysis of PW, SA and PP in air.

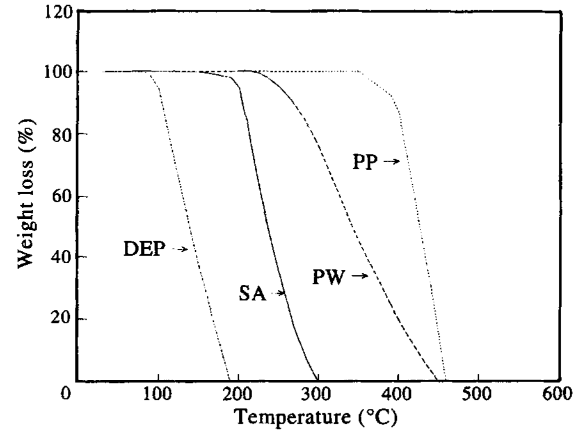

Fig. 2. TG analysis of DEP, SA, PW and PP in air.

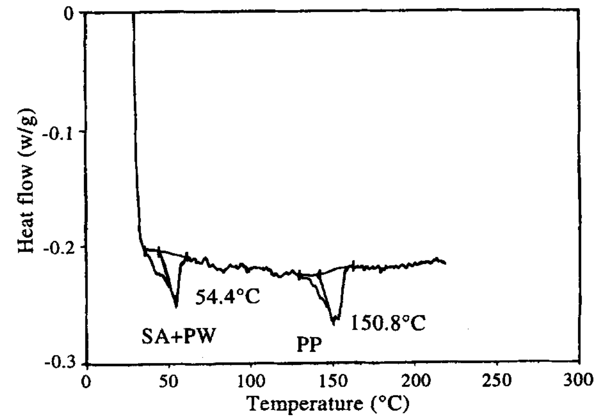

Fig. 3. DSC analysis of binders in air. Binders were mixed with silicon nitride powders before test.

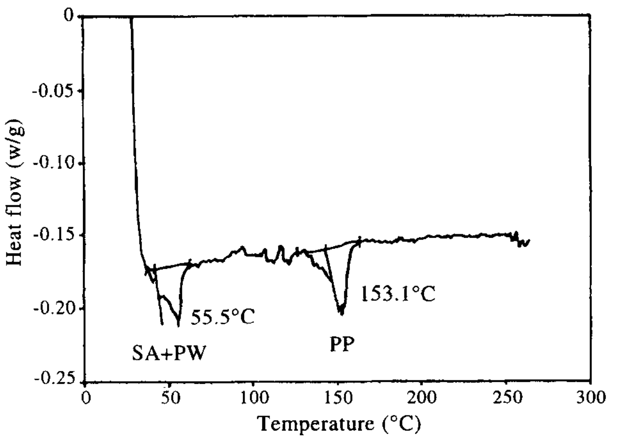

Fig. 4. DSC analysis of binders in nitrogen. Binders were mixed with silicon nitride powders before test.

decomposition temperatures of DEP, SA, PW and PP were invariably lower in air than in a nitrogen atmosphere (Figs 5 and 6). The IR analysis revealed that the major bonds in the binder system were C–H and C = O.

3.2 The effects of the atmosphere on thermal debinding

The porosity of samples during thermal debinding under an air, nitrogen and mixture of $N_2/5\%H_2$, respectively, were determined at different temperatures, as shown in Fig. 7. The results indicated that the rate of extracting binders was in the order of air > $N_2/5\%H_2$ > nitrogen. It was previously reported that the oxidation of low-molecular-weight binders were apt to decompose in air than in nitrogen to form a network of pore channels.[9–12]

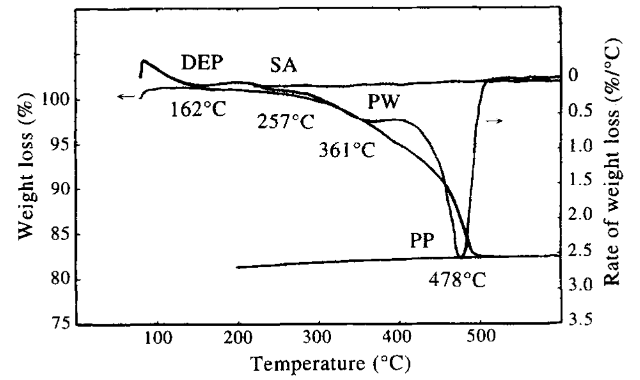

Fig. 6. TG analysis of binders in nitrogen with a heating rate of 10°C min^{-1}.

The results in Fig. 7 also showed that a relatively greater temperature (~450°C) was required in nitrogen to remove binders completely than in the air (400°C). It was previously reported that the high-molecular-weight binders (PW and PP) were easier to remove in air because of the continuous oxygen supply.[9] A higher temperature required in nitrogen was probably because chain scission, thermal decomposition and evaporation process were involved.[9,12,13] The results of weight loss vs. temperature also illustrated a greater binder removing rate in air than in nitrogen (Fig. 8).

The IR spectra of binders at various thermal debinding temperatures under air, nitrogen, and $N_2/5\%H_2$ are illustrated in Fig. 9(a)–(c). Major peaks were detected in the ranges of 1300–1500 cm^{-1}, 1700–1800 cm^{-1}, and 2800–3100 cm^{-1} in specimens at room temperature. The peaks in the range of 1700–1800 cm^{-1} indicate C = O bonds in DEP and SA. The peaks in the other two ranges represent the C–H bonds.

As the debinding temperature was increased to 200°C in air, the C = O peaks disappeared (Fig. 9(a)). This indicated that the low-molecular-weight binders (DEP and SA) could have been burned out in air at this temperature. This observation was different from samples debinded in nitrogen and $N_2/5\%H_2$ atmospheres, however (Fig. 9(b) and (c)), in which the C = O bonds still remained. It suggested that some of SA still remained.

As the debinding temperature was increased to 250°C, the C = O peaks appeared again in samples

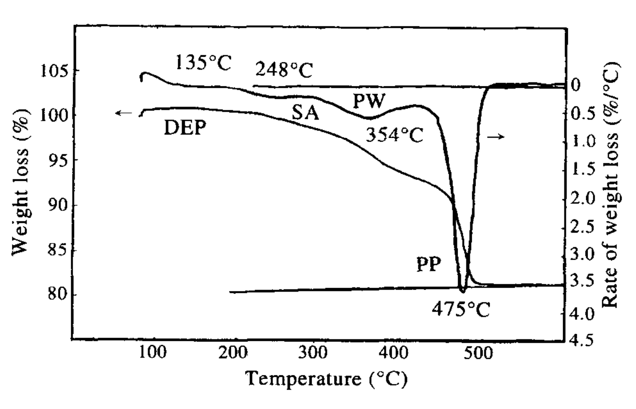

Fig. 5. TG analysis of binder system in air with a heating rate of 10°C min^{-1}

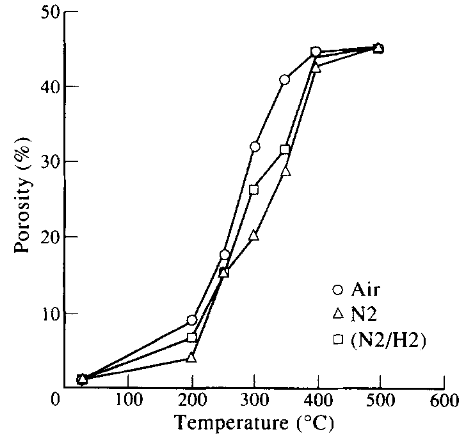

Fig. 7. Porosity vs. thermal debinding temperature in three different atmospheres.

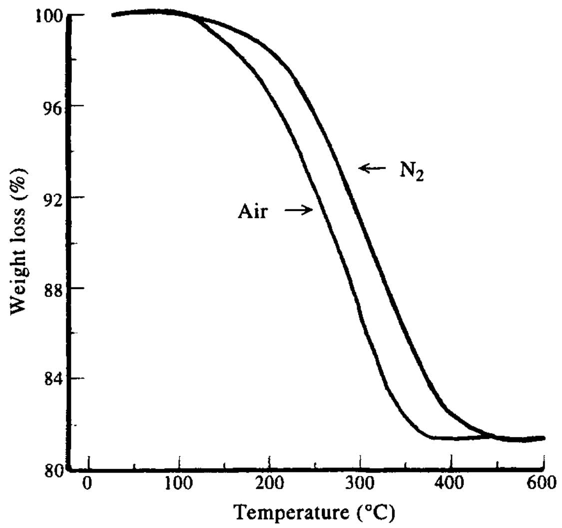

Fig. 8. TG analysis showing the percentage of binder decomposition in air and nitrogen atmosphere.

debinded in air. The reason for the observation of $C=O$ peaks was probably owing to the formation of hydroperoxide groups from polypropylene.[13,14] No $C=O$ peaks were detected in nitrogen or $N_2/5\%H_2$ atmospheres at temperatures exceeding 250°C. Instead of forming $C=O$ peaks, the C–H bonds were detected in the range of 1700–1800 cm^{-1} in N_2/H_2 atmosphere at 250–300°C. This probably could be explained by the thermal decomposition and reduction of DEP and SA. All peaks became weaker as the temperature increased, and decomposed by 500°C.

The pore size distribution of samples after thermal debinding in air, nitrogen and $N_2/5\%H_2$ atmospheres at different temperatures was measured by mercury porosimetry as shown in Fig. 10(a)–(c). The pore volume apparently increased with debinding temperature. In order to show the changes in pore size distribution at various temperatures, the distribution of pores in Fig. 10(a)–(c) were divided into two groups by their sizes (0.01–0.05 μm and 0.05–0.10 μm), and plotted against the debinding temperature (Fig. 11). The proportion of large pores, as opposed to the distribution of small pores, increased and then decreased with the debinding temperature. Similar results were observed in samples debinded under air, N_2 or $N_2/5\%H_2$ atmospheres.

The results in Fig. 11, along with the DSC and TG analysis, provide useful information on the removal rate of small (DEP and SA) and large-molecular-weight (PW) binders at various temperatures. The results in Fig. 11 indicate that the debinding rate in N_2 or $N_2/5\%H_2$ atmospheres was apparently lower than in the air. In addition, a smaller maximum pore size was reached at greater temperatures while debinding in N_2 or N_2/H_2 in comparison with air.

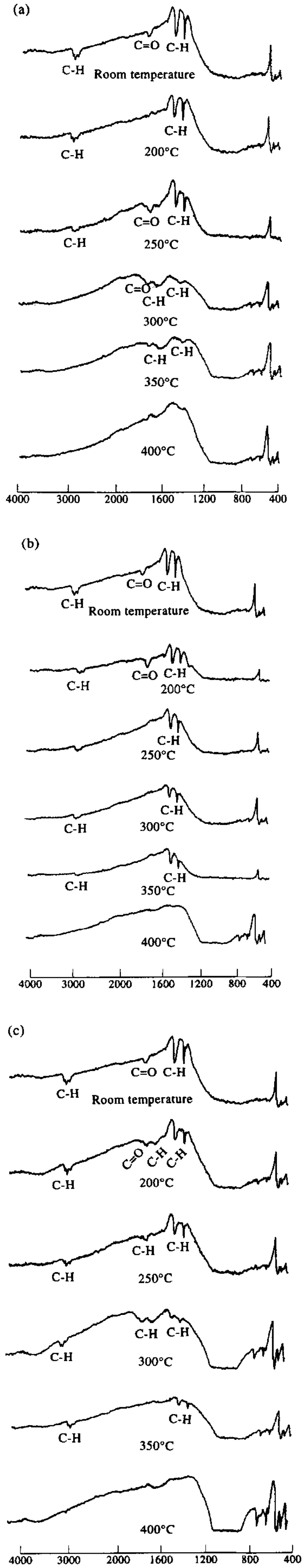

Fig. 9. IR analysis at various thermal debinding temperatures in (a) air, (b) nitrogen, and (c) ($N_2/5\%H_2$).

3.3 Density and strength

The density and strength of sintered Si_3N_4 containing 55 vol% solid loading are listed in Table 1. Both the density and strength are in the order of $N_2 > N_2 + 5\%H_2 >$ air. This suggested that a slow binder removal rate and debinding atmosphere are essential to the sintered properties.

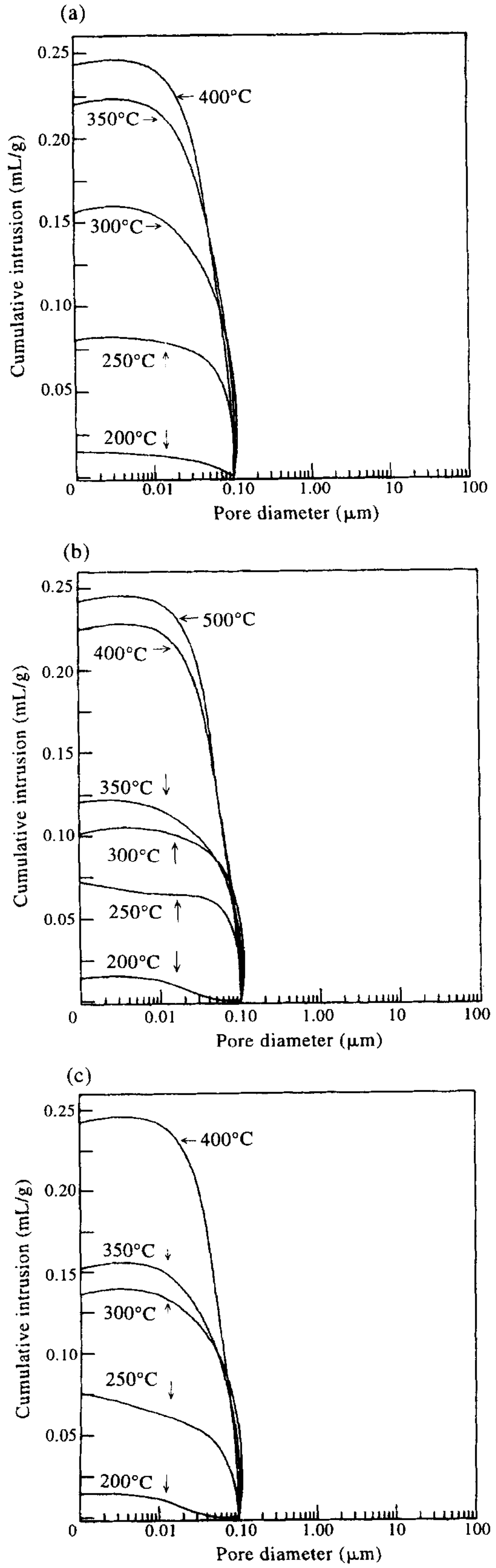

Fig. 10. Pore-size distribution of silicon nitride components at different thermal debinding temperatures in (a) air, (b) nitrogen, and (c) $(N_2/5\%H_2)$.

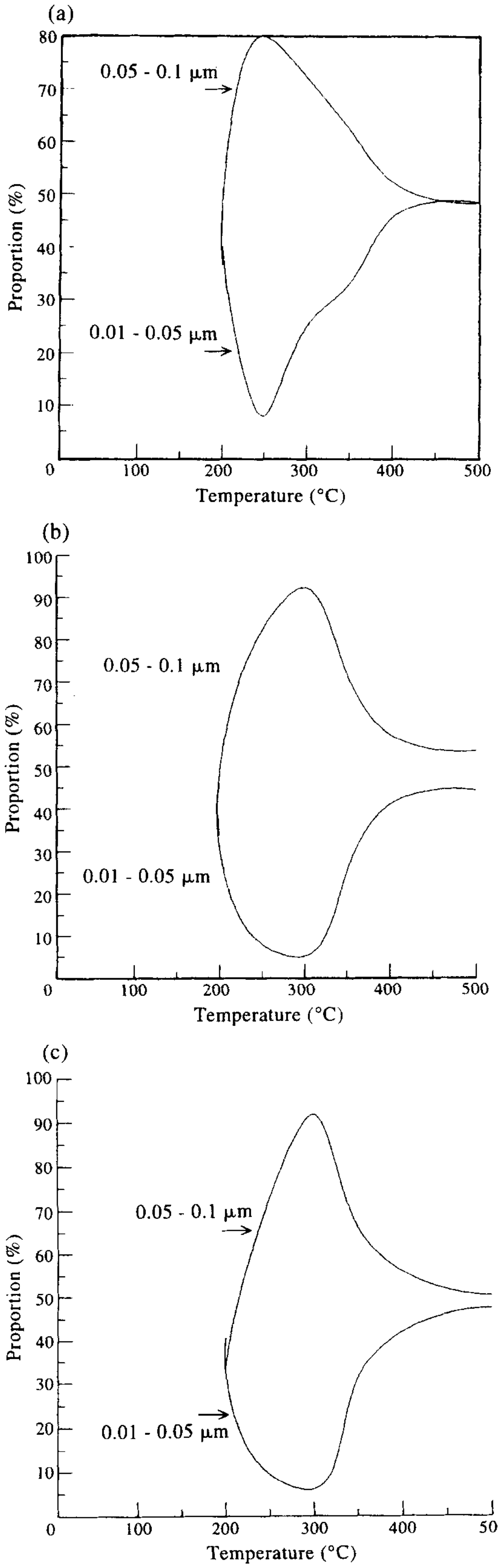

Fig. 11. The proportion of large and small pores in silicon nitride components at different thermal debinding temperatures in (a) air, (b) nitrogen, and (c) $(N_2/5\%H_2)$.

Table 1. The density and strength of sintered silicon nitride under different debinding atmospheres

Atmosphere	N_2	N_2+5%H_2	Air
Density (%TD)	95.5	94.8	93.5
Strength (MPa)	750	710	580

4 SUMMARY AND CONCLUSIONS

1. The softening points of stearic acid, paraffin wax and polypropylene decreased after mixing with ceramic powders.
2. The softening points and thermal decomposition temperatures of stearic acid, paraffin wax and polypropylene were consistently lower in air than in nitrogen.
3. The debinding rate of Si_3N_4 under different atmospheres was in the order of air $> N_2 + 5\%H_2 >$ nitrogen. The density and strength were, however, in an opposite order, i.e. nitrogen $> N_2 + 5\%H_2 >$ air.
4. The bonding structure and thermal decomposition of binders strongly depended on the thermal debinding temperature and the atmosphere.

ACKNOWLEDGEMENT

The authors would like to thank the National Science Council, Taiwan, R.O.C. for financial support of this study under Contract No. NSC 84-2216-E-006-055.

REFERENCES

1. QUACKENBUSH, C. L., FRENCH, K. & NEIL, J. T., *Ceram. Eng. Sci. Proc.*, **3**(1-6) (1982) 20–34.
2. INOUE, M., KIHARA, Y. & ARAKIDA, Y., *Interceramics*, **2** (1989) 53–57.
3. EDIRISINGHE, M. J. & MCCOLLUM, J. I., *Ceram. Int.*, **19** (1993) 113–120.
4. HENS, K. F., LEE, D., LIN, S. T. & GERMAN, R. M., *Powder Metall. Int.*, **23**(1) (1991) 15–21.
5. GERMAN, R. M. & HENS, K. F., *Ceram. Bull.*, **70**(8) (1991) 1294–1302.
6. EDIRISINGHE, M. J., *Ceram. Int.*, **17** (1991) 89–96.
7. STRIVENS, M. A., *Am. Ceram. Soc., Bull.*, **42**(1) (1963) 13–19.
8. TAKAHASHI, M., HAYASHI, J., SUZUKI, S. & SHIGURE, Y., *J. Mater. Sci.*, **27** (1992) 5297–5302.
9. WRIGHT, J. K. & EVANS, J. R. G., *J. Mater. Sci.*, **26** (1991) 4897–4904.
10. SHUKLA, V. N. & HILL, D. C., *J. Am. Ceram. Soc.*, **72**(10) (1989) 1797–1803.
11. GERMAN, R. M., *Am. Powder Metall. Inst.*, **23**(4) (1987) 237–245.
12. MASIA, S., CALVERT, P. D., RHINE, W. E. & BROWEN, H. K., *J. Mater. Sci.*, **24** (1989) 1907–1912.
13. TZOGANAKIS, C., TANG, Y., VLACHOPOULOS, J. & HAMIELEC, A. E., *Polym.-Plast. Technol. Eng.*, **28**(3) (1989) 319–350.
14. GIJSMAN, P. & HENNEKES, J., *Polym. Degrad. Stab.*, **42** (1993) 95–105.