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Interaction between binder and powder in injection moulding of alumina

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In injection moulding of alumina the binder components interacted with the alumina powder by a Lewis acid–base reaction. Among the binder components used, stearic acid played a major role in determining the process behaviour even though its composition was only 4 wt% of the total binder (1.8 vol% of the formulation including powder). The effects of the chemisorbed stearic acid due to the Lewis acid–base interaction were a reduction of the apparent viscosity by a factor of 20, minimized separation of binder from the powder during moulding, but a higher content of binder burnout residue than in the carbonyl–iron system.

1. Introduction

Powder injection moulding is a manufacturing process capable of producing high performance and complex shaped ceramics, metals and carbides at low cost [1]. The method is comprised of the following major steps: mixing, moulding, debinding and sintering. Among these steps, mixing, moulding and debinding involve the interaction of binder and powder. Therefore, the binder chemistry has a major influence on the success of the process. The selection of a binder composition has been empirical and often the same binder composition is applied to different powders. In such cases any difficulty encountered in mixing or moulding due to an incompatible binder and powder system is frequently attributed to the shape factor or size of the powder. Actually, several different binder systems can be used in this process, with the oil- or wax-based binders being most common [2]. The typical oil- or wax-based binder consists of a major filler of oil or wax, a backbone polymer, a plasticizer and a surface active agent. However, the composition is not restricted to four components as one component can play different roles. For example, for a binder composed of polystyrene and vegetable oil (40–70 wt% oil) [3], the vegetable oil acts as the major filler, the surface active agent and the plasticizer.

Generally speaking, compatibility of binder and powder means good wetting or strong adhesion. Usually, further extension of the non-adhering end of the surfactant into the polymer–wax mixture in addition to the adhesion of surfactant to powder surface is required to avoid a phase separation of binder from powder during injection moulding, where a high shear rate (in the range of $10^5\ s^{-1}$) usually occurs. Better adhesion between binder and powder enhances powder dispersion in the binder during mixing [4], increases the ideal powder loading for moulding by reducing the flow viscosity of the mixture [5] and yields better mechanical properties in the green state [6, 7]. On the other hand, a stronger adhesion between binder and powder raises the thermal pyrolysis temperatures of the binder [8] and gives rise to a larger amount of binder burnout residue [8, 9]. As adhesion by Van der Waals forces is very weak, adhesion between binder and powder is primarily achieved by hydrogen bonding through a Lewis acid–base reaction [6] or by covalent bonding [7, 10, 11]. Usually, a small molecular weight component is used as a surface active agent in the binder formulation. Such an agent has a functional group that adheres to the particle surface and an oriented molecular chain that extends into the binder matrix. It serves as a bridge between the binder and powder. In addition, it can also serve as a lubricant reducing the friction between powder and machine/die walls, improve dispersion of powder in binder and enhance miscibility between binder components [12]. For adhesion through covalent bonding, small molecular weight titanate or silane alkoxides are often used as the coupling agents. Nevertheless, it is difficult to predict the effects of such organo-metallics due to the non-congruent effects on flow viscosity [11]. Additionally, a strong coupling agent coating on the powder surface can block the passway of decomposed binder and cause debinding defects [13]. Furthermore, the decomposition products of these inorganic materials are composed of carbon, metal oxides and metal carbides, which makes them suitable only for some specific powder systems, such as silicon carbide or nitride.

Hydrogen bonding involves the reaction of an acid (electron acceptor) and a base (electron donor). The average acid–base characteristic of a powder surface is determined by the point of zero charge, which is approximated by the value of the isoelectric point [14]. The isoelectric points for some typical oxide ceramics have been documented [14–16]. A powder with an isoelectric point of less than 7 is considered to have an average acidic surface, and vice versa. For organic materials the strength of the acid–base characteristic is determined by the "solvent shift" of the functional groups involved in forming the acid–base complexes by using infrared (i.r.) spectroscopy [17, 18]. Generally, the acid–base characteristics of organic materials can be estimated from their functional groups. For example, organic materials with functional groups of ether (C–O–C) or carbonyl (C=O) are basic, while organic materials with a hydroxyl (O–H) functional group are acidic. In a similar manner, the interaction occurring between a ceramic powder and an organic binder can be recognized by observing the shifting of I.R. absorption peaks of the key functional groups. Such approaches have been used to identify the interaction of binders with ceramic powders, and to quantify the evolution of binder burnout residue [8, 9].

2. Experimental procedure

The powder used in this study was alumina, whose isoelectric point measured using both mass transport and micro-electrophoresis, was 9.2 [19]. The powder was doped with 0.1 wt % MgO in the form of a magnesium nitrate water solution. The slurry was dried and calcined at 800 °C for 2 h. The powder was milled and sieved with a 170 mesh screen (90 μm) before mixing with the binder. The multicomponent binder was derived from a system suggested by Wiech [20]. It consisted of polypropylene, paraffin wax, carnauba wax and stearic acid. Table I shows the composition of this binder and some respective properties of each component. Additionally, a binder without the addition of stearic acid was also used for comparison. In this case, the binder composition was 0.70 weight fraction of paraffin wax instead of 0.66 weight fraction of paraffin wax and 0.04 weight fraction of stearic acid.

Polypropylene was the backbone polymer, and it contributed to the strength in debinding. Paraffin wax has a low flow viscosity, and was the major component. Both polypropylene and paraffin wax are nonpolar organic materials, whereas carnauba wax and stearic acid are polar organic materials. Carnauba wax is a strong and brittle organic composed of mostly organic esters (85%), and minor amounts of acids (4%), alcohol (3%) and impurities [21]. Stearic acid can serve as a plasticizer for polymers, as a lubricant between powder and machine/die walls, and as a surfactant between powder and binder [12]. Fig. 1 shows the thermal pyrolysis profiles of these four components tested in air. Only carnauba wax showed a burnout residue higher than 1 wt % at a temperature higher than 500 °C.

TABLE I Binder composition and characteristics of each component

	Weight fraction	Density ($g\,cm^{-3}$)	Molecular weight ($g\,mol^{-1}$)	Melting point (°C)
Polypropylene	0.20	0.890	43 000	147
Paraffin wax	0.66	0.900	350–420	59
Carnauba wax	0.10	0.995	1300–1500	84
Stearic acid	0.04	0.941	285	74

The feedstock for injection moulding was prepared with a double-planetary mixer. It has a fractional powder loading of 0.56. The binder components were added in one batch without special efforts to coat stearic acid on the alumina powder. The flow viscosity of the blend was measured using an Instron capillary rheometer 50.9 mm long and 1.27 mm in diameter, while that of binder was measured using a Haake rotating cone viscometer. Rectangular bending specimens with the dimensions of 63.22 × 12.60 × 3.14 mm were formed with a 22 ton Battenfeld reciprocating screw injection moulding machine instrumented with a feedback controller. The homogeneity of the moulded specimen was determined based on the weight fraction of powder in different positions of the injection moulded specimen. Thermal gravimetric analysis (TGA), with an accuracy of ± 0.01 mg, was used to determine the thermal pyrolysis of binder components and measure the weight ratio of powder: binder in the moulded specimen. The moulded specimens were debound either by solvent extraction, using heptane as solvent [22], or thermal extraction with an alumina wicking powder [23]. The residual carbon contents of the debound specimens were measured using combustion analysis.

The interaction between the binder components and powder was monitored using I.R. spectroscopy. The absorption spectrum of the molecular bonds was recorded in the form of wave numbers, which is the reciprocal value of the wavelength (cm). The value of the wave number was varied between 800 and 4000 cm^{-1}. The specimens were prepared in the form of a thin film with the addition of KBr, which diluted the concentration of the tested material and enhanced film formation. The wave number of the absorption peak of KBr was lower than 400 cm^{-1}, so it did not interfere with the absorption pattern of interest [24].

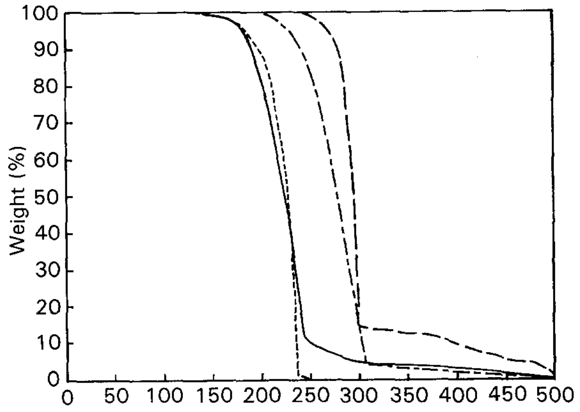

Figure 1 Thermal pyrolysis of binder components tested in air (10 K min^{-1}). ——, Stearic acid; — — — , carnauba wax; — — — — , polypropylene; - - - - , paraffin wax.

The intensity change and the wave number shift of the absorption peaks were used as an indication of the change of the molecular bonding states.

3. Results and discussion

3.1. Interaction

The I.R. absorption spectra of stearic acid and stearic acid mixed with alumina powder, and carnauba wax mixed with alumina powder are shown in Figs 2 and 3, respectively. The assignments of the individual bonds for the ester, acid and alcohol functional groups are shown in Table II [25]. After mixing with alumina powder, the relative intensity of the absorption peaks at 1380 and 3200 cm^{-1} increased significantly with respect to the other peaks. As the shift in wave number for the carbonyl group (C=O) was usually less than 30 cm^{-1} after forming an acid–base complex [17], the peak at 1380 cm^{-1} was explained as the result of shifting the O–H bending peak from 1470 or 1510 cm^{-1}. For acidic polymers the acidic strength was determined by determining the shifting of the O–H stretching peak after forming an acid–base complex with a basic solvent [18]. The quantity of wave number change from about 3600 cm^{-1} to lower wave numbers was related to the energy of the acid–base reaction. The acidic functional groups of stearic acid and carnauba wax partially existed in a hydrogen bonded state before mixing with the alumina powder. Thus, changes in the relative intensity to the lower wave numbers (or lower energy states) of O–H stretching and bending after mixing indicated the formation of new hydrogen bonds. For carnauba wax there was no significant change in the absorption intensity arising from the interaction of alumina powder with the functional groups of carbonyl (C=O) and ether (C–O–C).

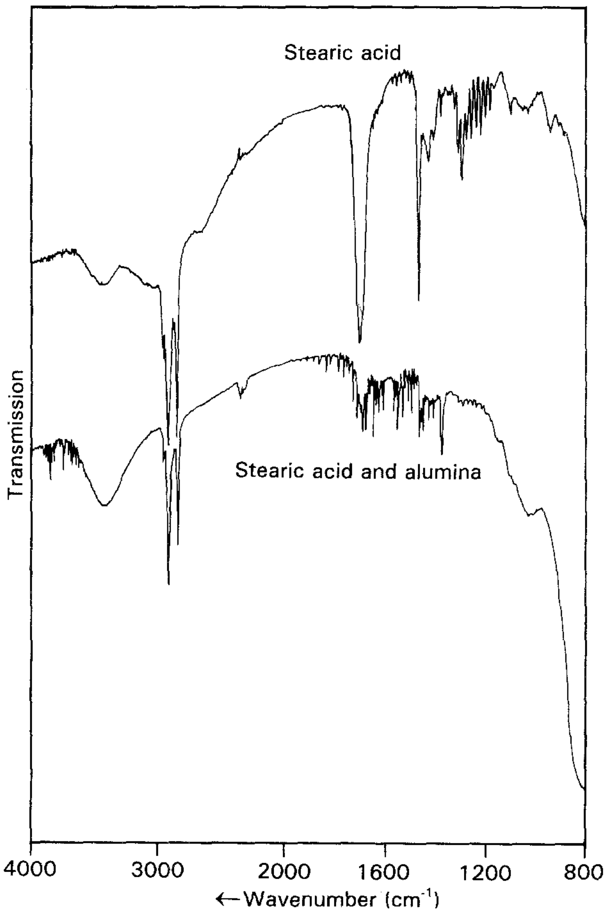

Figure 2 I.r. spectra of stearic acid and stearic acid mixed with alumina powder.

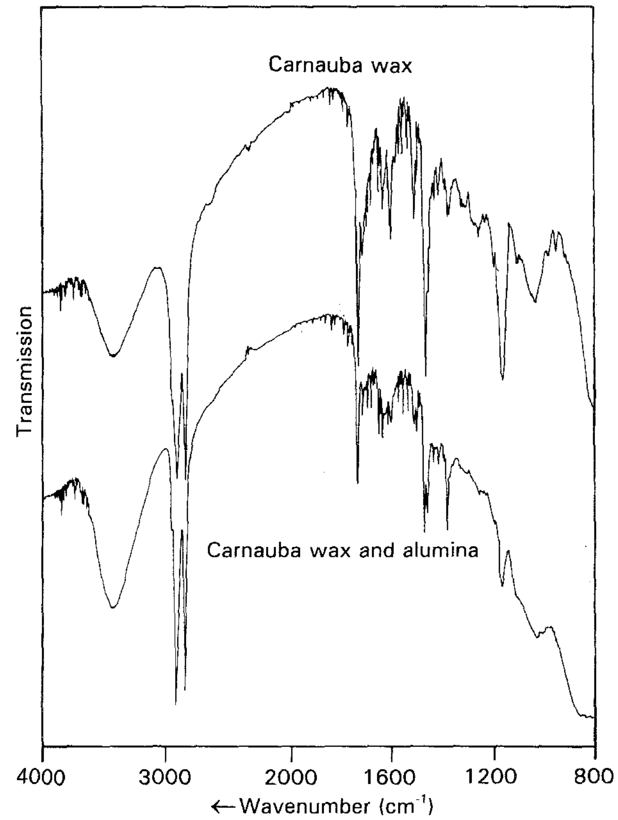

Figure 3 I.r. spectra of carnauba wax and carnauba wax mixed with alumina powder.

TABLE II Assignments of the i.r. absorption peaks for the polar bonds of stearic acid and carnauba wax [25]

Bond	Wave number (cm^{-1})
C–O–C stretching	1170
C–O stretching	1200–1300
O–H bending	1470, 1510
C=O stretching	1700, 1730
O–H stretching	3200

A strong interaction between a single binder component and the powder did not necessarily imply a strong interaction between the component and the powder when the component was mixed with the other components [6]. This component may have had a stronger affinity toward the other components. The i.r. absorption spectra of binder and binder mixed with alumina powder are shown in Fig. 4. Again, the relative intensity of the absorption peaks at 1380 and 3200 cm^{-1} increased significantly with respect to the other peaks. Therefore, the interaction between binder and alumina powder arose primarily from the bonding between hydrogen of the carboxylic functional group and the basic surface sites of the alumina

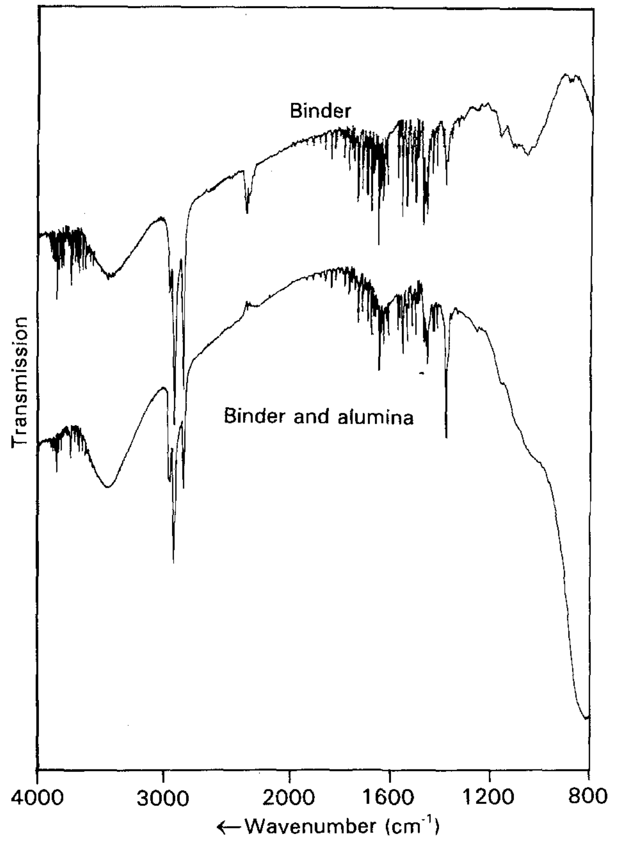

Figure 4 I.r. spectra of binder and binder mixed with alumina powder.

powder. The observation was the result of a Lewis acid–base reaction.

Different explanations of the interaction between binder and alumina powder have been proposed based on an acidic alumina surface. The interaction between poly(vinyl butyral) and alumina arose from both the carbonyl and hydroxyl functional groups, where the C=O stretching peak shifted to a lower wave number by 20 cm^{-1} and the intensity of the O–H stretching peak increased [9]. However, only the interaction occurring between the alumina powder and the carbonyl group, but not the hydroxyl group, was explained [9]. As the tested specimens were contaminated with solvent during sample preparation, interaction between poly(vinyl butyral) and the residual solvent could have induced the shifting of the C=O stretching peak and the broadening of the O–H stretching peak. This argument was supported by the observation that different I.R. absorption spectra were recorded when the specimens were prepared with different solvents, i.e. solvents containing hydroxyl (methanol and ethanol) and solvent containing carbonyl (methyl ethyl ketone) or ether (tetra hydrofuran) [9]. In a similar manner, due to the increased intensity of the carboxylate peak during binder pyrolysis, the interaction between poly (methyl methacrylate) and alumina was initially expected to take place between oxygen of the newly formed carboxylate (O–C–O) and aluminium on the alumina surface [8]. However, this explanation was dubious since a new carboxylate absorption peak was also observed during binder pyrolysis in the other powders such as glass and diamond [8]. The existence of the new carboxylate peak for the mixture of poly (methyl methacrylate) and diamond (a non-ionic solid) indicated that the carboxylate peak was independent of the interaction between binder and powder. Oxidation of polymer during pyrolysis could have caused the increased intensity of the carboxylate peak, as scission of the polymer chain by oxidation resulted in the formation of carboxylate in the transitional state [26].

3.2. Effects of interaction

Due to hydrogen bonding, the binding strength of polyethylene to aluminium (with an oxide surface) was enhanced by up to 24% when stearic acid was used as the surface active agent [27]. In this research, a bulky mixture of powder and binder was difficult to obtain without the addition of stearic acid in the binder. Such surface adhesion also reduced the flow viscosity of the powder–binder blends. Fig. 5 shows the modification of the melt flow viscosity with 4 wt % stearic acid replacing paraffin wax in the binder composition. The melt flow viscosity was reduced by a factor of about 20 with the substitution of 4 wt % paraffin wax by stearic acid in the binder composition. Stearic acid could have behaved as a plasticizer for the binder and reduced the flow viscosity of the binder. However, its effect on reducing the viscosity of binder was minimal (0.018–0.015 Pa at 150 °C) when 4 wt % stearic acid replaced paraffin wax in the binder. As the inherent binder viscosity was much lower than that of the powder–binder blend, the resistance to flow was caused mainly by interparticle friction and friction between the powder and the capillary wall. Therefore, the significant viscosity reduction of powder–binder mixture was due to the strongly preferred adhesion of stearic acid to the powder surface. Such a reduction of viscosity accounted for the reduction of iron pickup arising from the machine wear during mixing [28]. A similar ten-fold reduction of the flow viscosity was observed by surface coating calcium carbonate powder with stearic acid in polystyrene [29]. Presumably, hydrogen bonding occurred between the acidic hydroxyl functional group and the basic calcium carbonate powder surface. On the other hand, the viscosity was reduced by a factor of less than 2 when

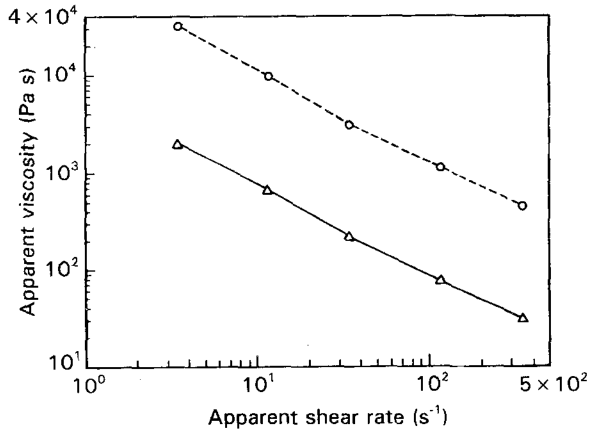

Figure 5 Apparent viscosity versus apparent shear rate at 150° C for blends with a powder loading of 0.56, showing the reduction of melt flow viscosity with 4 wt % stearic acid replacing 4 wt % paraffin wax in the binder. Stearic acid (wt %): △——△, 4; ○- - - -○, 0.

TABLE III Residual carbon contents (p.p.m.) for different debinding conditions

Debind route	Pyrolysis atmosphere	Maximum hold temperature (°C)	Hold time (h)	Residual carbon (p.p.m.)
Solvent	Oxygen	500	1	480
Solvent	Oxygen	1000	1	320
Solvent	Air	500	1	550
Solvent	Air	1000	1	330
Solvent	Air	1000	2	300
Solvent	Hydrogen	500	1	960
Thermal	Air	500	1	440

10 wt % of stearic acid replaced polyethylene in injection moulding carbonyl iron powder [30]. The flow viscosity of polyethylene was reduced by a similar factor with the addition of 10 wt % stearic acid. In this case, reduction of the melt flow viscosity was due primarily to the plasticization of polyethylene by stearic acid and not due to surface interactions, because the carbonyl iron powder ideally had a non-polar surface.

A strong adhesion between binder and powder also minimized the separation of binder from powder during moulding. A dilatant flow behaviour was believed to cause an inconsistent flow with binder separating from the powder under high shear rates [31]. The mixture used in this study behaved as a pesudoplastic with a yielded stress in the injection moulding temperature range (7.5 kPa at 150 °C) [32]. Fig. 6 shows the TGA profiles for different locations of the injection moulded specimen. Within the sensitivity of the equipment, the final weight percentages of powder for these three locations were the same. The non-overlapping behaviour in the region of maximum rate of weight loss was a result of different initial test weights of specimens. Although a high pressure was used to mould such a high viscosity blend into a thin and long rectangular part, there was no separation of binder from the powder. However, binder separating from the powder was observed in moulding carbonyl iron powder with a similar binder composition [33], even though the mixture had a similar non-dilatant pseudoplastic flow with a yield stress. This reflected the lack of strong bonding in the moulding of carbonyl iron.

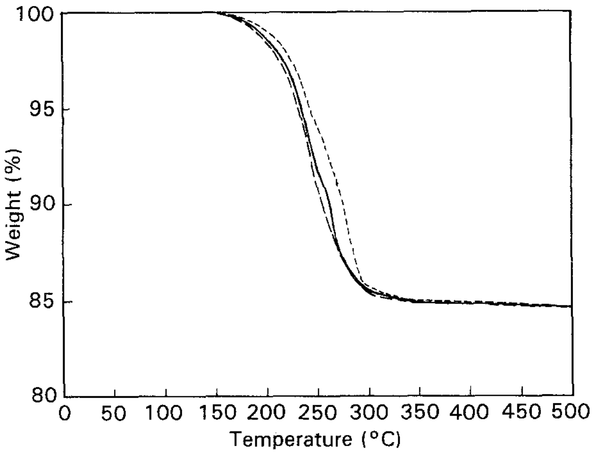

Figure 6 TGA profiles of samples cut from the different sections of rectangular injection moulded specimen (10 K min^{-1} in air). ——, Gate, 44.985 mg; – – – –, centre, 58.032 mg; — — —, end, 40.762 mg.

Interactions among binder components resulted in a high content of binder burnout residue, as cross-linking of organic materials enhanced the carburization during thermal pyrolysis [34]. As shown in Fig. 1, the polar carnauba wax and stearic acid yielded larger amounts of burnout residues than polypropylene, even though their molecular weights were much lower than polypropylene. Similarly, a strong interaction between these components with the alumina surface resulted in a high content of binder burnout residue. Table III shows the residual carbon contents for different debinding conditions, with debinding in hydrogen atmosphere yielding the maximum residual carbon content; the lowest residual carbon was about 300 p.p.m., obtained by holding the debound specimens at 1000 °C for 2 h in air before sintering. This value was much higher than the 20 p.p.m. level obtained after debinding injection moulded Fe–2 %Ni (initial carbon = 0.89 wt %) with a similar binder composition (only 1 wt % of stearic acid) in a hydrogen atmosphere [35]. As the residual carbon reacted with alumina and formed volatile species at temperature higher than 1500 °C [36], such a high content of residual carbon in the alumina resulted in deteriorated sintered properties. For example, the flexural strength decreased from 389 to 336 MPa when the residual carbon content increased from 300 to 550 p.p.m. [32]. In terms of oxidation behaviour, carbon formed by the thermal degradation of poly(vinyl butyral) in alumina was about five times more reactive than graphite [37]. Since the reaction of free carbon with hydrogen or oxygen was thermodynamically favourable in the temperature range of interest [38], the different carbon retention behaviour between alumina powder and carbonyl iron powder reflected the differing surface interactions with the binder. Such an argument is supported by the observation of different residual carbon contents after pyrolysis for poly (vinyl butyral) mixed with different ceramic powders [39], in which a powder having an ioselectric point close to 7 (neutral) catalysed the decomposition of poly(vinyl butyral) and yielded a low carbon content, while the acidic or basic powders had a strong adhesion to the polymer and yielded a higher residual carbon content. As the powder surface behaved more acidic or basic, the higher was the residual carbon content. However, the decomposition of binder catalysed by alumina was not very effective since alumina powders having different surface areas (9.5 and 0.22 $m^2 g^{-1}$) showed very similar debinding behaviours [40].

4. Conclusions

The interactions between polar binder components and the surface of alumina powder has been identified with i.r. absorption spectra. The interaction occurred by a Lewis acid–base reaction with the hydroxyl of acidic organic materials adhering to the oxygen sites on the alumina surface. No significant interaction arose from the ester functional group of carnauba wax. The surface characteristics (or polarity) of alumina favoured the addition of a small amount of stearic acid:binder to reduce the melt flow viscosity and minimize the separation of binder from the powder during moulding. However, the content of the binder burnout residue increased. With less polar powder surfaces the benefit from stearic acid was reduced and was probably associated more with changes in binder viscosity.

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References

1. R. M. GERMAN, in "Powder injection molding" (Metal Powder Industries Federation, Princeton, NJ, 1990) p. 5.
2. R. M. GERMAN, K. F. HENS and S. T. LIN, *Bull. Amer. Ceram. Soc.* **70** (1991) 1294.
3. K. F. HENS, D. LEE, S. T. LIN and R. M. GERMAN *Powder Metallurgy Int.* **23** (1990) 15.
4. M. D. SACKS, C. S. KHADILKAR, G. W. SCHEIFFELE, A. V. SHENOY, J. H. DOW and R. S. SHEU, in "Ceramic powder science", edited by G. L. Messing, K. S. Kazdiyasni, J. W. McCauley and R. A. Harber (American Ceramic Society, OH, 1987) p. 495.
5. M. T. MARTYN, R. J. JAMES, and B. HAWORTH, *Metal Powder Report* **43** (1988) 816.
6. F. M. FOWKES, in "Ceramic powder science", edited by G. L. Messing, K. S. Kazdiyasni, J. W. McCauley and R. A. Harber (American Ceramic Society, OH, 1987) p. 411.
7. J. G. ZHANG, M .J. EDIRISINGHE and J. R. G. EVANS, *J. Mater. Sci.* **23** (1988) 2115.
8. Y. N. SUN, M .D. SACKS and J. W. WILLIAMS, in "Ceramic powder science II" Vol. I, Part A, edited by G. L. Messing, E. R. Fuller Jr and H. Hausner (American Ceramic Society, OH, 1988) p. 538.
9. K. E. HOWARD, C. D. E. LAKEMAN and D. A. PAYNE, *J. Amer. Ceram. Soc.* **73** (1990) 2543.
10. M. GREEN, T. KRAMER, M. PARISH, J. FOX, R. LALANANDHAM, W. RHINE, S. BARCLAY, P. CALVERT and H. K. BOWEN, in "Ceramic powder science", edited by G. L. Messing, K. S. Kazdiyasni, J. W. McCauley and R. A. Harber (American Ceramic Society, OH, 1987) p. 449.
11. K. LINDQVIST, E. CARLSTROM, M. PERSSON and R. CARLSSON, *J. Amer. Ceram. Soc.* **72** (1989) 99.
12. M. J. EDIRISINGHE, *Ceram. Int.* **17** (1991) 89.
13. *Idem, J. Mat. Sci. Lett.* **9** (1990) 1039.
14. J. S. REED, in "Introduction to the principles of ceramic processing" (John Wiley & Sons, New York, 1988) p. 134.
15. R. O. JAMES, in "Ceramic powder science", edited by G. L. Messing, K. S. Kazdiyasni, J. W. McCauley and R. A. Harber (American Ceramic Society, OH, 1987) p. 349.
16. R. H. YOON, T. SALMAN and G. DONNAY, *J. Colloid Interface Sci.* **70** (1979) 483.
17. F. W. FOWKES and D. O. TISCHLER, *J. Polym. Sci. Polym. Chem. Edn* **22** (1984) 547.
18. T. K. KWEI, E. M. PEARCE, F. REN and J. P. CHEN, *J. Polym. Sci. B, Polym. Phys.* **24** (1986) 1597.
19. E. M. DELISO, A. S. RAO and W. R. CANNON, in "Ceramic powder science", edited by G. L. Messing, K. S. Kazdiyasni, J. W. McCauley and R. A. Harber (American Ceramic Society, OH, 1987) p. 525.
20. R. E. WIECH, US Patent #4,661,315, April (1987).
21. H. BENNET, in "Industrial wax", Vol. I (Chemical Publishing Company Inc., New York, 1963) p. 43.
22. S. T. LIN and R. M. GERMAN, *Powder Metall. Int.* **21** (1989) 19.
23. T. S. WEI and R. M. GERMAN, *Int. J. Powder Metall.* **24** (1988) 327.
24. H. H. WILLARD, L. L. MERRITT Jr, J. A. DEAN and F. A. SETTLE Jr, in "Instrumental methods of analysis ", 6th Edn (D. Van Nostrand Company, New York, 1981) p. 148.
25. A. L. SMITH, in "Applied infrared spectroscopy, fundamentals, techniques, and analytical problem-solving" (John Wiley & Sons, New York, 1979) p. 287.
26. J. K. WRIGHT, J. R. G. EVANS and M. J. EDIRISINGHE, *J. Amer. Ceram. Soc.* **72** (1989) 1822.
27. H. SCHONHORN, *J. Polym. Sci. A* **1** (196) 2335.
28. J. G. ZHANG, M. J. EDIRISINGHE and J. R. G. EVANS, *Ind. Ceram.* **9** (1989) 72.
29. Y. SUETSUGU and J. L. WHITE, *J. Appl. Polym. Sci.* **28** (1983) 1481.
30. B. J. CARPENTER, M.S. Thesis, Rensselaer Polytechnic Institute, Troy, NY (1988).
31. M. J. EDIRISINGHE, H. M. SHAW and K. L. TOMKINS, *Ceram. Int.* **18** (1992) 193.
32. S. T. PAUL LIN, PhD Thesis, Rensselaer Polytechnic Institute, Troy, NY (1991).
33. B. O. RHEE, M. Y. CAO, H. R. ZHANG and C. I. CHUNG, presented at MPIF, APMI Powder Metallurgy Conference and Exhibition, June, 1991, Chicago, IL.
34. W. K. SHIH, M. D. SACKS, G. W. SCHEIFFELE, Y. N. SUN and J. W. WILLIAMS, in "Ceramic powder science II," Vol. I, Part A, edited by G. L. Messing, E. R. Fuller Jr and H. Hausner (American Ceramic Society, OH, 1988) p. 549.
35. S. T. LIN, R. M. GERMAN, K. F. HENS and D. LEE, in "Advances in powder metallurgy", Vol. 3, edited by E. R. Andreotti and P. J. McGeehan (Metal Powder Industries Federation, NJ, 1990) p. 423.
36. F. J. KLUNG, W. D. PASCO and M. P. BOROM, *J. Amer. Ceram. Soc.* **65** (1982) 619.
37. M . V. BODDU and D. S. VISWANATH, *J. Amer. Ceram. Soc.* **73** (1990) 1620.
38. D. R. GASKELL, in "Introduction to metallurgical thermodynamics" (McGraw Hill Book Company, New York, 1981) p. 585.
39. S. MASIA, P. D. CALVERT, W. E. RHINE and H. K. BOWEN, *J. Mater. Sci.* **24** (1989) 1907.
40. J. R. G. EVANS and M. J. EDIRISINGHE, *J. Mater. Sci.* **26** (1991) 2081.

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