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Practical Experiences with Some Principles Pertinent to CIM

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Abstract

Ceramic injection moulding (CIM) is a promising manufacturing process which attracts growing attention today. The basic principles pertinent to CIM are well known, but as there is a variety of viable manufacturing approaches the final results may be quite different. This paper highlights some practical experience with specific aspects of CIM.

One requirement of the binder system is that its components must be chemically compatible with respect to ceramic powders. Stearic acid, a very popular binder constituent, may react with some ceramic powders and seriously disturb the process. A solution to this problem is presented.

The imprints of knock out pins on injection moulded ceramic products may show flaws. The origin of and how to remedy this flaw type is discussed.

Defect sensitivity is a major issue with ceramics. As well as other ceramic forming processes the injection moulding process may cause specific defects. Fracture strength of injection moulded silicon carbide is compared with data from literature. Some measures to improve the quality are discussed.

1 Introduction

The principles associated with the powder injection moulding process are today well covered in review articles[1–4] and books.[5,6] However because of the proprietary sphere in which the process is operated, information on practical experience is still rather scarce. This article will focus on experience with three CIM principles. The first treated principle is related to the statement: 'The powders and the binder must be chemically passive with respect to each other'.[7] Our experience with this principle concerning the use of stearic acid with a particular ceramic powder is described in Section 2. In Section 3 a particular source of defects, caused by tooling characteristics is treated as an illustration of the principle: '... many factors related to tooling and moulding machines ... influence the success of P.I.M.'[8] The mechanical properties of ceramic components are strongly influenced by the presence of agglomerates, big porosities and other defects. In Section 4 we treat the influence of these parameters on the strength of silicon carbide arriving at the conclusion: 'Defect sensitivity is a major issue with P.I.M. ceramics'.[9]

2 Chemical Reaction between Binder Component and Powder May Cause Defects

Among the processing aids for thermoplastic binders stearic acid is widely used.[5] It lowers the surface energy of the powder–binder interface and decreases, even at low concentrations, the viscosity of the compound. Stearic acid also promotes mould release of the components. In spite of these interesting features stearic acid may cause severe problems when used in combination with yttrium oxide, an important sintering aid for silicon nitride ceramics. Figure 1 shows silicon nitride test beams (for bending strength measurement) after binder removal. Typical deformations which are accompanied with internal cracks are explicit.

The deformations suggest flow patterns of injection moulding. Therefore at first erroneously a solution has been sought in optimizing injection moulding parameters. By systematic omission of sintering aids and binder constituents in the compound it could be demonstrated that deformation only occurred when yttrium oxide and stearic acid were both present. It is known that yttrium oxide

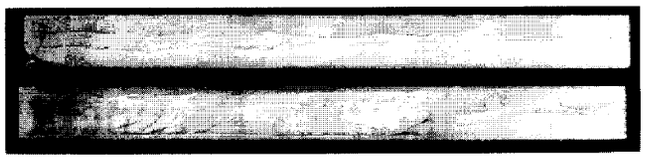

Fig. 1. Silicon nitride test beams after binder removal with typical deformations.

may react with weak acids. Stearic acid is thought to react as follows:

$$Y_2O_3 + 6C_{17}H_{35}COOH \rightarrow 2(C_{17}H_{35}COO)_3Y + 3H_2O \quad (1)$$

X-ray diffraction (XRD) analysis on samples after binder burn-out was not sensitive enough to confirm this. Mixtures have been made of only stearic acid and yttrium oxide in a weight ratio of 16/1. After thermal treatment for 1 h in air at 170°, 210 and 240°C respectively, XRD patterns have been made. They are shown in Fig. 2. In the mixture treated at 240°C the typical peak for yttrium oxide completely disappears. More detailed gravimetric and infrared analysis confirmed that reaction (1) started at 210°C and is completed at 240°C. In

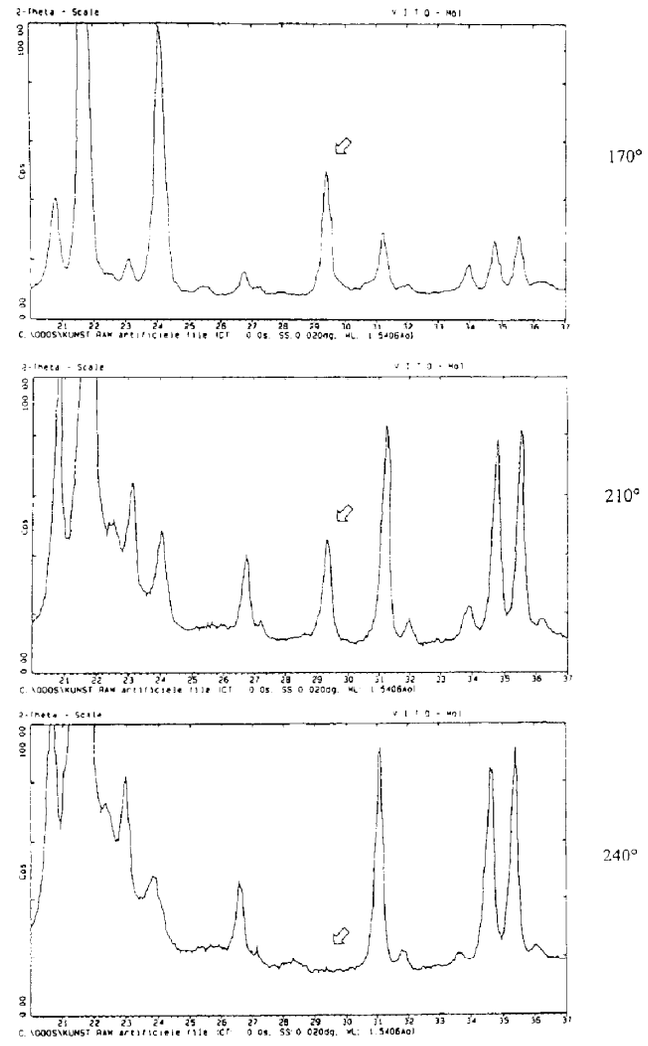

Fig. 2. X-ray diffraction patterns of yttrium oxide–stearic acid mixtures treated during 1 h in an oxidizing atmosphere at different temperatures. Arrow indicates Y_2O_3.

our CIM process these temperatures are not reached during mixing (170°C) and only a temperature of 200°C is momentarily reached during injection moulding. It is assumed that during thermal binder removal yttrium oxide is partially converted into yttrium stearate. Apparently the presence of yttrium stearate promotes relaxation of injection moulding stresses. The same typical deformation during binder removal can be induced by mixing 2 wt% of zinc stearate in a compound without yttrium oxide.

A solution to the problem has been found in altering the burn-out conditions. The binder in components containing yttrium oxide and stearic acid can be flawlessly removed by changing from an oxidizing furnace atmosphere to an inert one. In these conditions reaction (1) does not occur.

3 Flaws on the Imprints of Knock Out Pins

When injection moulding ceramic products, binder removal flaws often appear originating from the imprints of knock out pins. This phenomenon has been investigated for the production of silicon nitride beams for bending tests. As shown on Fig. 3 the flaws generally follow the circumference of the imprint and sometimes break away. Almost any automatically produced ceramic product shows such imprints and it is obvious that the accompanying flaws cannot be tolerated.

At first it was thought that the flaws originated during ejection when the knock out pins push the hardly solidified product out of the mould cavity. A number of test beams were manually removed without using the knock out pins. Nevertheless these beams were still flawed after binder removal. Also the influence of storing conditions on flaw formation has been examined. A short time period between injection moulding and binder removal is beneficial to avoid flaw formation. Also dry storing conditions lowered the frequency of flaw occurrence. None of these conditions however could completely avoid flaw formation.

The origin of the flaws appeared to be a lack of rigidity of the mould. At the maximum injection pressure the support plate bent considerably. The modular build-up of the cavity plate lowered the stiffness of the mould and aggravated the phenomenon of flaw formation. As the knock out pins are supported independently in the ejector housing, a relative displacement between cavity wall and knock out pins is possible. This movement initiated the flaw formation according to the series of events shown in Fig. 4.

By adding support pillars to the most solicited zones, the mould became more rigid and all visible flaws disappeared completely.

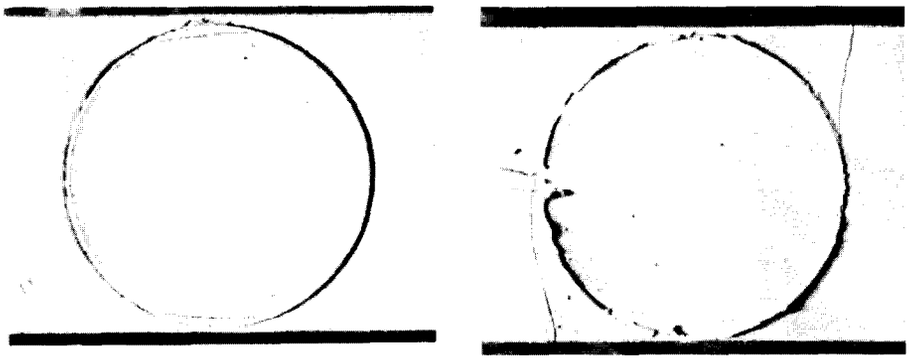

Fig. 3. Flaws on imprints of knock out pins.

4 Fracture Strength of Injection Moulded Silicon Carbide

4.1 Introduction

The strength of ceramics depends to a large extent on defects introduced during the manufacturing process. During the production of ceramics, minimising the formation of such process-related defects, requires thorough process control. Power injection moulding may introduce specific defects which will reflect on strength. For injection moulded silicon carbide the dependence of strength on some process variations has been examined. The results are compared with data from commercial products and from the literature.

4.2 Experimental procedure

An α-SiC powder (Lonza, type UF15) has been used for the following work. The powder contained a significant number of strong agglomerates. Therefore, the powder was milled for one hour in a planetary mill equipped with tungsten carbide jars and balls. As sintering aids 2·5% carbon and 0·6% boron carbide were added before milling. The dried powders were compounded with a thermoplastic binder in an oil-heated Z blade mixer. Flexural test bars (5·3 × 4·1 × 61·2 mm) were injection moulded (Arburg Allr. 220-90-350) with the granulated material using a mould with a double cavity. The binder was removed by thermal degradation in a nitrogen atmosphere. Pressureless sintering was carried out in a graphite furnace at 2150°C for one hour. Four-point bending strength was measured at room temperature on the as-sintered test bars. At least 26 test bars were tested per batch. Testing was conducted with a crosshead speed of 0·5 mm per minute.

In an attempt to reduce process-related flaws three different processes have been investigated. Table 1 gives an overview.

For the baseline material (a) the milled and dried powder was directly compounded and conventionally moulded

Table 1. Processing variants

Process steps	*a*	*b*	*c*
Milling in acetone	x	x	–
Milling in water + 2% PEG	–	–	x
Sieving slurry over 10 μm sieve	–	–	x
Spray drying	–	–	x
Air drying	x	x	–
Compounding with binder; volume %	20·5	20·5	21·5
Injection moulding over 0·3 mm filter	–	x	–
Injection moulding without filter	x	–	x

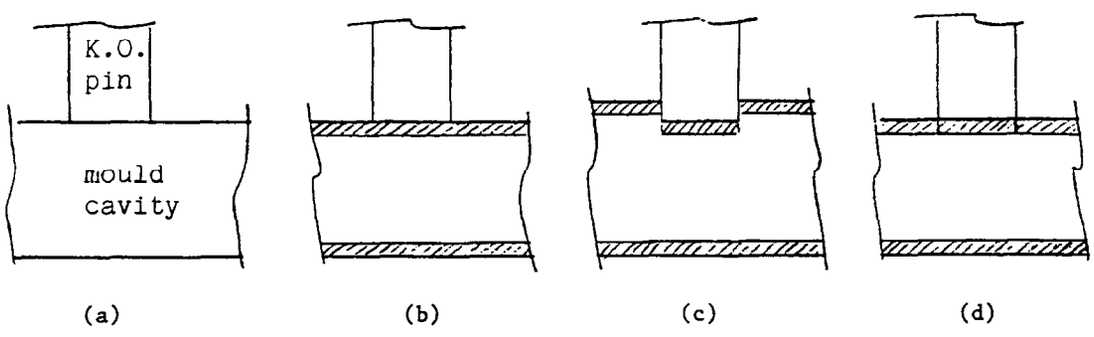

Fig. 4. Crack initiation at imprints of knock out pins: (a) situation before injection; (b) the mould cavity fills with feedstock; solidification starts immediately at cold mould wall; (c) at complete filling the mould pressure is maximum; the mould wall is displaced because of lack of rigidity of the mould; the knock out pin shears the solidified compound layer; (d) when the mould pressure drops the wall returns to its initial position; the pressure in the compound is still high enough to restore the initial surface but because of the lack of plasticity in the outer layer the origin for a flaw is made; the flaw is invisible on the as-moulded samples but emerges on binder removal.

Fig. 5. Silicon nitride filtering element provided with 0·3 mm laser cut holes.

The (b) material was prepared as the baseline material but it was injection moulded through a filtering element. The injection unit of the Arburg may be equipped with a steel filtering element. As the holes of this element are fairly large (0.75 mm) and as it was feared that the compound might pick up iron contamination, the steel element was replaced by a ceramic one. Figure 5 shows this filtering element. It is made of pressure-sintered silicon nitride and the holes of 0.3 mm are cut by laser.

In the (c) variant the milled slurry was filtered over a plastic filter cloth with very fine pores. In order to force the slurry through such a fine filter it has to be in a well-deflocculated state. As this is difficult when using an organic liquid, the milling medium was replaced by water. After filtering the slurry was spray dried. In order to improve agglomeration on spray drying 2% of polyethylene glycol was added.

5 Results

The sintered density of moulded material after processing variants (a) and the (b) was 98·3% of T.D. The (c) material had a density of 97·3% of T.D.

Table 2 gives fracture strength values for the three materials. For comparison some data supplied for commercial products and data from the literature are also tabulated. The baseline material (a) shows a mean strength of 475 MPa. Only the HIPped material from Dutta[10] (510–580 MPa) and the annealed injection moulded material from Whalen[12] (483 MPa) show higher mean strengths. However, the resulting Weibull modulus of 6·4 is low. The fracture origins of the weakest samples

Table 2. Fracture strength of the (a), (b) and (c) SiC material compared with commercial products and data from the literature

	Type of product	*Mean strength (MPa)*	*Minimum strength (MPa)*	*Maximum strength (MPa)*	*Weibull modulus*
VITO					
Baseline material (a)	Injection moulding	475	294	588	6·4
Injection moulded through filter (b)	Injection moulding	468	366	546	9·4
Moulded after filtering the powder suspension (c)	Injection moulding	491	289	648	6·5
Commercial products					
Feldmühle	CD110	350			4
Schunck Dyko	SSiC	400			4
Gimex	Pressureless sintering	420			10
Data from literature					
Dutta[10]	Dry pressing	350	295	405	
	Slurry pressing	430	360	500	
	HIP Ta	580			
	HIP glass	510			
Seshadri[11]	Dry pressing	395	230	560	
	Injection moulding	338	265	410	
Whalen[12]	Injection moulding	455		546	
	After annealing	483		543	
Butt[13]	CRB 210 Coors siliconized	365			
	Hexalon carbor B doped	447			
	Al SASC-ESK Al doped	368			

are mostly large pores of about 100 μm. No contaminants could be detected in the vicinity of the pores. The material moulded after processing variant (b) shows almost the same mean strength (468 MPa) as the first material (a). However the Weibull modulus is better (9·4). The origin of the failure for the weakest samples are pores with a diameter of 50–60 μm. It is assumed that by passing the compound through the moulding filter, air pockets are stretched out and redistributed into smaller unities being less harmful.

The material moulded after processing variant (c) shows a slightly higher mean strength (491 MPa). Also the high maximum strength of 648 MPa indicates that by sieving the starting material many of the potential failure origins are removed. Nevertheless, the Weibull modulus is only a little higher than for the baseline material. Fractography showed that flaws typical for poor injection moulding quality were found as fracture origin in the weakest samples. This was not surprising because this batch showed a very large increase in viscosity. Table 1 shows that the binder content has been raised by 1% but it was still difficult to mould. The reason for this is undoubtedly the presence of 2% polyethylene glycol in the spray-dried powder. This product seems to be incompatible with the binder used for injection moulding. If this problem could be solved better results would be expected.

6 Conclusions

Injection moulded silicon carbide test bars have been produced which show, in the as-sintered state, a very acceptable mean strength, compared with material produced by other techniques. Moulding through a 0·3 mm filter seems to yield better Weibull modulus values. When working with screened material (10 μm) a better strength was obtained but this manufacturing route was hampered by an incompatibility of the binder with a spray drying aid.

References

1. Edirisinghe, M. J. & Evans, J. R. G., Review: Fabrication of Engineering Ceramics by Injection Moulding I, Materials Selection. *Int. J. High Technol. Ceram.*, **2** (1986) 1–31.
2. Edirisinghe, M. J. & Evans, J. R. G., Review: Fabrication of Engineering Ceramics by Injection Moulding II, Techniques. *Int. J. High Technol. Ceram.*, **2** (1986) 249–278.
3. Iocacca, R. G., A Critical Assessment of Characterization Tests needed to support Powder Injection Moulding Component Fabrication, *Rev. in Part. Mat.*, **2** (1994), 269–314.
4. German, R. M., The Importance of Particle Characteristics in Powder Injection Molding, *Rev. in Part. Mat.*, Vol. 1, 1993, pp. 109–160.
5. German, R. M., *Powder Injection Molding*. Metal Powder Industries Federation, Princeton, New Jersey, 1990.
6. Mutsuddy, B. C. & Ford, R. G., *Ceramic Injection Molding*. Chapman and Hall Ltd, 1994.
7. Ref. 5, p. 138.
8. Ref. 5, p. 176.
9. Ref. 5, p. 459.
10. Dutta, S., Effect of various consolidation techniques on microstructure, strength and reliability of alpha-SiC, *Silicon Carbide '87 — Ceramic Transactions, A. Cer. S.*, Vol. 2, 1987, pp. 202–214.
11. Seshadri, S. G., Srinivasan, M. & Chia, K. Y., Microstructure and mechanical properties of pressureless sintered alpha-SiC, *Silicon Carbide '87 — Ceramic Transactions, A. Cer. S.*, Vol. 2, 1987, pp. 215–226.
12. Whalen, T. J. & Bear, J. R., Improved silicon carbide for advanced heat engines. Part II: Pressureless sintering and mechanical properties of injection molded silicon carbide, *Silicon Carbide '87 — Ceramic Transactions, A. Cer. S.*, Vol. 2, 1987, pp. 355–663.
13. Butt, D. P., Tressler, R. E. & Spear, K. E., Corrosion of SiC materials in N_2–H_2–CO gaseous environments — durability and mechanical properties. *J. Am. Ceram. Soc.*, **75** (1992) 3268–3277.