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The production of Mn–Zn ferrite ceramics by injection moulding

A. J. PIGRAM, R. FREER
Materials Science Centre, University of Manchester/UMIST, Grosvenor Street, Manchester M1 7HS, UK

A ceramic injection-moulding technique has been used for the preparation of bars and toroids of Mn–Zn ferrite. The binders were based on a combination of polypropylene, microcrystalline wax and stearic acid. Components up to 4 mm thick were fabricated; extended binder burn-out schedules, up to 8.5 days in duration, in a nitrogen atmosphere were required for the thicker parts. Sintered densities were typically 90% of the theoretical value. Initial permeabilities of the toroids were lower than expected (700–1600 rather than 4000) due to the smaller grain size (4–6 μm) of the fired products. Optimization of the sintering schedule should enable the microstructure and magnetic properties to be improved.

1. Introduction

Ferrites are ceramic materials based on iron oxide [1]. Their importance comes from the fact that they exhibit soft magnetism, which enables their usage in a wide range of applications. There are three main types of ferrite currently produced in large quantities: Mn–Zn ferrite, Ni–Zn ferrite and Mg–Zn ferrite. These are used for applications as diverse as radio antennae, transformer cores and microwave waveguides [1].

Most ferrites are commercially produced by a mixed oxide route, using a small amount of organic binder, dry pressing, and sintering in line kilns or batch kilns. In recent years a number of alternative preparation routes have been applied to the production of ferrite powder, for example co-precipitation [2, 3] (which is now used commercially) and sol–gel processing [4].

Injection moulding is an alternative forming process which involves heating a charge of thermoplastic material to a consistent state of fluidity, transferring it under pressure through channels to an enclosed space, and then cooling to produce a solid part with the greatest possible degree of homogeneity [5]. Ceramic injection moulding is of interest as it offers the potential for the near net shape production of complex designs. Currently, such shapes are prepared by the joining of two or more sections, and there are obvious advantages in being able to produce single-section specimens. Ceramic injection moulding has been successfully used for the production of ceramics with high density, and mechanical strengths that compare well with those of conventionally produced ceramics [6–9]. However, no work has been reported on the fabrication of magnetic ceramics using the injection moulding technique. In this study, the production of Mn–Zn ferrite ceramic plaques and toroids of composition equivalent to $Mn_{0.558}Zn_{0.372}Fe_{2.07}O_4$ is reported. The binders employed were based on the work of Edirisinghe [10] (combinations of polypropylene, microcrystalline wax and stearic acid). The magnetic properties of the sintered products and their dependence on microstructure are discussed.

2. Experimental procedure

The starting materials used for the production of Mn–Zn ferrite were commercial-grade powders: Fe_2O_3 (Sidmar Chemicals grade 015), ZnO (Durham Chemicals grade N5) and MnO (Meclenna/Chemical grade HP).

Prior to injection moulding, the powders were processed in a conventional manner: batches of powder to yield 5 kg of Mn–Zn ferrite were weighed out and wet-mixed with 2 l of water and 125 cm^3 of Dispex in a Torrance IS attritor mill (containing 1 cm diameter stainless steel balls) for 1 h. The slurry was removed from the mill and dried in an oven for 18 h at 120 °C. The resultant solid was crushed using a pestle and mortar, and passed through a 2 mm mesh sieve. The powder was weighed into 1.2 kg batches, placed in metal boats and calcined. Samples were heated at $\sim$ 10 °C min^{-1} to 860 °C for 2 h, and cooled naturally with the oven over a period of hours. After calcining, the powder was milled with 1 l of water and 125 cm^3 of Dispex in the attritor mill for 90 min. The powder was removed from the mill and dried at 120 °C for 18 h. The resultant solid was again crushed using a pestle and mortar, and passed through a 35 μm mesh sieve to produce a fine powder.

For injection moulding the sieved powder was divided into batches of 650 g. Two binder formulations were used:

(i) Mix 1 comprised 7 parts polypropylene, 1 part microcrystalline wax, and 1 part stearic acid.

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(ii) Mix 2 comprised 6 parts polypropylene, 2 parts microcrystalline wax, and 1 part stearic acid.

The polypropylene was supplied by Atochem (Coathylene PY0787) and the microcrystalline wax was obtained from Okerin (1860Q).

Binder of each formulation, total weight 176 g, was added to the batches of ferrite powder. Initial mixing was performed in a soft plastic container by hand. Thorough mixing was then facilitated by use of a two-roll mill. The mill was initially operated with the front roller heated to 165 °C and the rear roller heated to 160 °C. When all the material had become attached to the rollers, the temperatures of the front and rear rollers were reduced to 160 and 155 °C, respectively. This caused all the material to become attached preferentially to the front roller. Mixing was achieved in the reservoir of material between the two rollers. Occasionally a knife was used to cut swathes of material which were inverted and placed on other areas of the roller, to encourage the mixing process in the reservoir. Mixing was complete after about 5 min.

Injection moulding was performed using a Negri–Bossi injection moulder (NB60). Small pieces (of irregular shape, with the largest dimension typically 2–3 cm) of the melted material (the melt) were put in a heated chamber (hot enough to melt the polypropylene, with the temperature varying from approximately 170 °C at the back of the chamber to 200 °C at the front). The screw thread rotated at approximately 100 r.p.m. and was drawn backwards approximately 9 cm in 30 s, leaving a void at the front which was filled by the melt.

The moulds used were in the shapes required to form plaques of 122 mm × 122 mm × 4 mm and 50 mm × 6 mm × 2 mm, and toroids of 20 mm outer diameter, 10 mm inner diameter and depth 2 or 4 mm. Mould temperatures were 30–110 °C and backing pressures of 0–70 bar were employed. Operating conditions for injection moulding are summarized in Table I. For the plaques, the moulds were designed such that the injection moulding nozzle fed the melt over a 1 mm deep gate into the mould. The gate between the sprue and the mould resulted in each specimen having a tab or flash upon removal from the sprue. This was subsequently removed using a scalpel. For the toroidal mould, a notch was made in the central spindle such that the specimen would be attached to the sprue by a 2 mm thick ring of material. The specimen could then be removed from the sprue by cutting round the sprue with a scalpel.

TABLE I Operating conditions of Negri–Bossi injection-moulding machine for the production of specimens 2 and 4 mm thick

Parameter	2 mm thick specimens	4 mm thick specimens
Nozzle temperature (°C)	190	200
Barrel temperature (front) (°C)	190	190
Barrel temperature (back) (°C)	170	180
Mould temperature (°C)	30	110
Backing pressure (bar)	Variable	70
Backing pressure time (s)	12	13
Cooling time before ejection (s)	55	55

Densities of the green specimens were determined from measurements of weight and dimensions. The flexure strength of injection moulded "green" plaques (50 mm × 6 mm × 2 mm) was determined in three-point loading configuration using an Instron 4301 operated at a crosshead speed of 0.5 mm min^{-1}. The lower supports were 35 mm apart.

Prior to binder burn-out, differential thermal analysis (DTA) was carried out on polypropylene, the major component of the binders (Seiko SSC/5200 simultaneous thermal analyser; specimen run in air, heating rate 5 °C min^{-1}). To provide further information about the degradation of the binder, hot-cell microscopy was used (Linkam THM600 hot stage with Olympus BH2 optical microscope); a small specimen (10 mm × 10 mm × 2 mm) was cut from a plaque and heated at a rate of 100 °C h^{-1} to 300 °C. The appearance of the specimen was noted at regular intervals.

Preliminary binder burn-out runs were performed on 2 mm thick plaques using heating rates of 30 °C h^{-1} at temperatures up to 150 °C, 6–10 °C h^{-1} for temperatures in the range 150–275 °C, and 30 °C h^{-1} at temperatures of 275–350 °C. For the thicker (4 mm) specimens (plaques and toroids) it was necessary to use different heating rates, and for certain temperature ranges the heating rate was as low as 1 °C h^{-1}. Binder burn-out was examined in static air (using a standard box furnace) and flowing nitrogen (using a tube furnace). After removal of the binder from the toroids, a number of specimens were sintered at 1320 °C. A variety of heating schedules were employed.

The densities of sintered toroids were determined by an immersion method using iodoethane. Selected specimens were ground and polished to 1 μm diamond paste and chemically etched in 52% HF for 15 s. Microstructures were studied by optical microscopy (using an Olympus BH2 microscope) and average grain sizes determined by the MLI method [11].

X-ray diffraction was performed using a Philips PW1380 diffractometer with horizontal goniometer. Data were compared with ASTM standard files. The initial permeability and loss factor for the toroids were determined by use of a Wayne-Kerr Multibridge, model 6425. Toroids were wound with 30 turns of cotton-coated copper wire and a 10 mV a.c. signal to 10 kHz applied. The series resistance, inductance and losses were measured.

3. Results

3.1. Production of plaques

The injection-moulded rectangular plaques varied in weight according to the backing pressure used; the effect of increasing the backing pressure is to pack the mould more efficiently, allowing more material into the mould. Densities of specimens prepared with the two binder mixes, using backing pressure of 0, 30, 50 and 70 bar, are shown in Table II. Specimens pre-

TABLE II Green-state densities of injection-moulded plaques (dimensions 50 mm × 6 mm × 2 mm)

Binder mix/backing pressure (bar)	No. of specimens	Density (g cm^{-3})	σ_{n-1}
1/0	9	2.263	0.025
1/30	7	2.330	0.030
1/50	8	2.349	0.021
1/70	9	2.355	0.023
2/0	10	2.297	0.020
2/30	14	2.377	0.041
2/50	16	2.400	0.017
2/70	15	2.406	0.017

pared with higher backing pressures exhibited higher green densities, indicating that the applied backing pressure enabled improved packing. On average, specimens prepared with binder of Mix 2 had green densities higher than those of specimens prepared with binder Mix 1 by 1.5–2.3%.

3.2. Green strength of plaques

Three-point flexure strength tests were performed on samples prepared with each level of backing pressure. The results are summarized in Fig. 1. It can be seen that the green strengths of specimens prepared with binder Mix 1 are significantly higher than those for specimens prepared with Mix 2. For each group of materials, the flexure strength is independent of applied backing pressure. However, all these flexure strengths are significantly higher than values usually obtained for spray-dried specimens, typically 0.2 MPa [12].

3.3. Binder burn-out for plaques

The results of DTA of polypropylene, performed in air, are shown in Fig. 2. A major endothermic peak occurred at 162 °C and exothermic peaks occurred at 393 and 422.2 °C. The two exothermic peaks are believed to reflect an oxidative reaction.

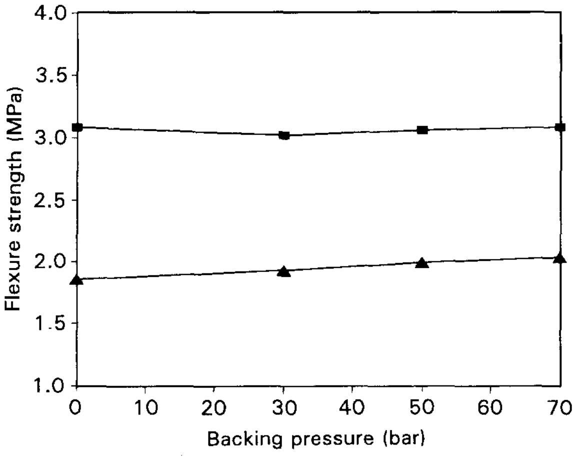

Figure 1 Flexure strength of green-state injection-moulded Mn–Zn ferrite specimens, prepared with (■) binder Mix 1 and (▲) binder Mix 2, as a function of backing pressure.

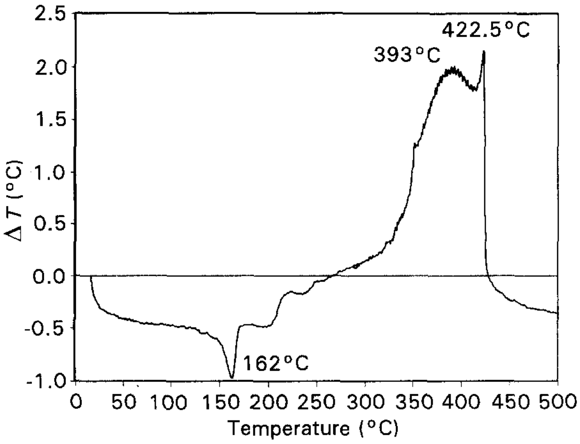

Figure 2 Differential thermal analysis of polypropylene, performed in static air with a heating rate of 5 °C min^{-1}.

Complementary hot-cell microscope studies of a section of injection-moulded plaque revealed a number of specific features as the specimen temperature was increased:

(i) up to 165 °C there was no noticeable change in the appearance of the specimen;

(ii) by 188 °C the specimen appeared wet;

(iii) by 200 °C there was rapid evolution of gas from the specimen, and the surface exhibited a mud-like texture;

(iv) by 250 °C the centre of the specimen had expanded and increased in height, and cracks were developing on the surface;

(v) by 270 °C the specimen exhibited significant cracking.

From these observations and from the DTA results (Fig. 2) it was initially concluded that there were no significant reactions occurring at temperatures below 162 °C. The reaction at 162 °C in Fig. 2 represents the melting of polypropylene. Polypropylene actually has a softening point of 150 °C. This was later found to be crucial. Above 162 °C the rate of evolution of gas depends upon the thickness of the specimen, and this in turn controls the maximum heating rate.

A number of trial binder burn-out runs were performed with 2 mm thick specimens. From these runs, the maximum safe heating rate for removing the binder, in static air, from the various specimens was determined. The results are summarized in Table III. At temperatures up to 150 °C (the softening point of the binder) specimens could be heated rapidly, at 30 °C h^{-1}; the critical temperature regime was 150–275 °C. Within this range, the maximum safe heating rate fell to 9 °C h^{-1} for specimens prepared with Mix 2 binder, and to 5–6 °C h^{-1} for those prepared with Mix 1 binder. Above 275 °C, both sets of specimens could again be heated at 30 °C h^{-1}. Hence, for specimens up to 2 mm thick, binder burn-out can be achieved in static air with heating rates in the range 5–30 °C h^{-1}. The extra, oxidative, reaction that occurs when processing in air was accompanied by shrinkage as binder was lost (the outer diameter

TABLE III Satisfactory binder burn-out rates in static air for injection-moulded ferrite plaques (50 mm × 6 mm × 2 mm)

Binder Mix No.	Backing pressure (bar)	Heating rate (°C h^{-1}) 150–275 °C	Heating rate (°C h^{-1}) 275–350 °C
1	0	6	30
	30	6	30
	50	5	30
	70	6	30
2	0	9	30
	30	9–10	30
	50	9–10	30
	70	9–10	30

shrank by 0.5 to 1.0 mm) but did not result in cracking or bloating of all specimens.

3.4. Binder burn-out from 4 mm thick specimens

An attempt was made to burn out the binder from 4 mm thick toroids (o.d. 20 mm, i.d. 10 mm) produced using Mix 2 binder. Mix 2 binder was used because it enabled a more rapid burn-out rate, but still imparted significant green strength to the specimens. Use of the binder burn-out schedule employed for 2 mm thick specimens (Table III) caused the toroids to disintegrate. An alternative schedule (comprising heating rates of 20 °C h^{-1} from 20 to 250 °C, 1 °C h^{-1} from 250 to 260 °C, hold for 10 h at 260 °C, 1 °C h^{-1} from 260 to 300 °C and 2 °C h^{-1} from 300 to 350 °C) resulted in surface defects (in the form of minor exfoliation) but the bulk of each specimen was undamaged. Such runs performed in static air showed that upto 300 °C the specimen surfaces were undamaged; by 350 °C, surface exfoliation had commenced. Further heating from 350 to 400 °C at 1 °C h^{-1} caused the specimen surface to exfoliate completely, resulting in the total removal of the surface layer. The exfoliation indicated a possible oxidative surface reaction. To minimize such problems, binder burn-out was attempted in a flowing nitrogen atmosphere using the schedule recommended by Edirisinghe [13] (Table IV). Performing this heat treatment in flowing nitrogen (4.5 l min^{-1}) enabled the binder to be successfully removed from the specimens without causing cracking, exfoliation or shrinkage of the toroids.

3.5. Sintering of toroids

A number of sintering runs were performed on specimens from which the binder had been removed according to the schedules listed in Table V. Toroids were heated in flowing air (4.6 l min^{-1}). During the first 300 °C of the cooling cycle the furnace atmosphere was changed to pure nitrogen according to a logarithmic relationship [14].

X-ray diffraction analysis of the toroids confirmed that they were single-phase ferrite. Optical micrographs of polished and etched specimens from runs 1–6 are shown in Fig. 3. Average grain sizes, specimen densities and magnetic properties of the sintered toroids are summarized in Table VI.

TABLE IV Binder burn-out schedule used for 4 mm thick toroids in flowing nitrogen (after Edirisinghe [13])

Temperature (°C)	Heating rate (°C h^{-1})/hold
RT–150	30
150	Hold for 24 h
150–350	2
350	Hold for 24 h
350–450	2

4. Discussion

The study demonstrated that ferrite ceramics can be prepared via injection moulding routes, but the processing is non-trivial and optimization of both component tools and production conditions is essential if good-quality products are to be obtained. For example, with the toroids, problems were encountered with the initial filling of the mould; several designs of toroid mould were investigated before complete mould filling was achieved. When the melt enters the mould the outer layer immediately solidifies. Shrinkage of the melt occurs as the thickness of this layer increases. The use of a hold pressure compensates for this shrinkage until the stage at which the sprue solidifies. If there is still liquid melt in the body it will solidify without the presence of the hold pressure, and will result in shrinkage leading to the creation of stresses within the body. This in turn will lead to the nucleation of voids or cracks. If air pockets remain within the body after sprue solidification then the moulded body will exhibit very poor properties. The use of a heated rear section to the mould is of some help in prolonging the time between the melt entering the mould and the surface layer solidifying; this helps to prevent incomplete mould filling. To ensure that no molten liquid remains after sprue solidification, the

TABLE V Sintering conditions of injection-moulded 4 mm thick toroids

Run No.	Heating conditions		Peak temperature
	Temperature (°C)	Heating rate (°C h^{-1})	(°C)/time (h)
1	20–800	80	
	800–1320	40	1320/2
2	20–520	45–47	
	520–1320	80	1320/2
3	20–520	45–47	
	520–1320	80	1320/4
4	20–520	45–47	
	520–1280	80	1280/2
5	20–520	46	
	520–1250	80	1250/4
6	20–520	46	
	520–1150	80	
	1150	1 h hold	
	1150–1320	80	1320/2
7	20–520	46	
	520–1050	80	
	1050	1 h hold	
	1050–1320	80	1320/2

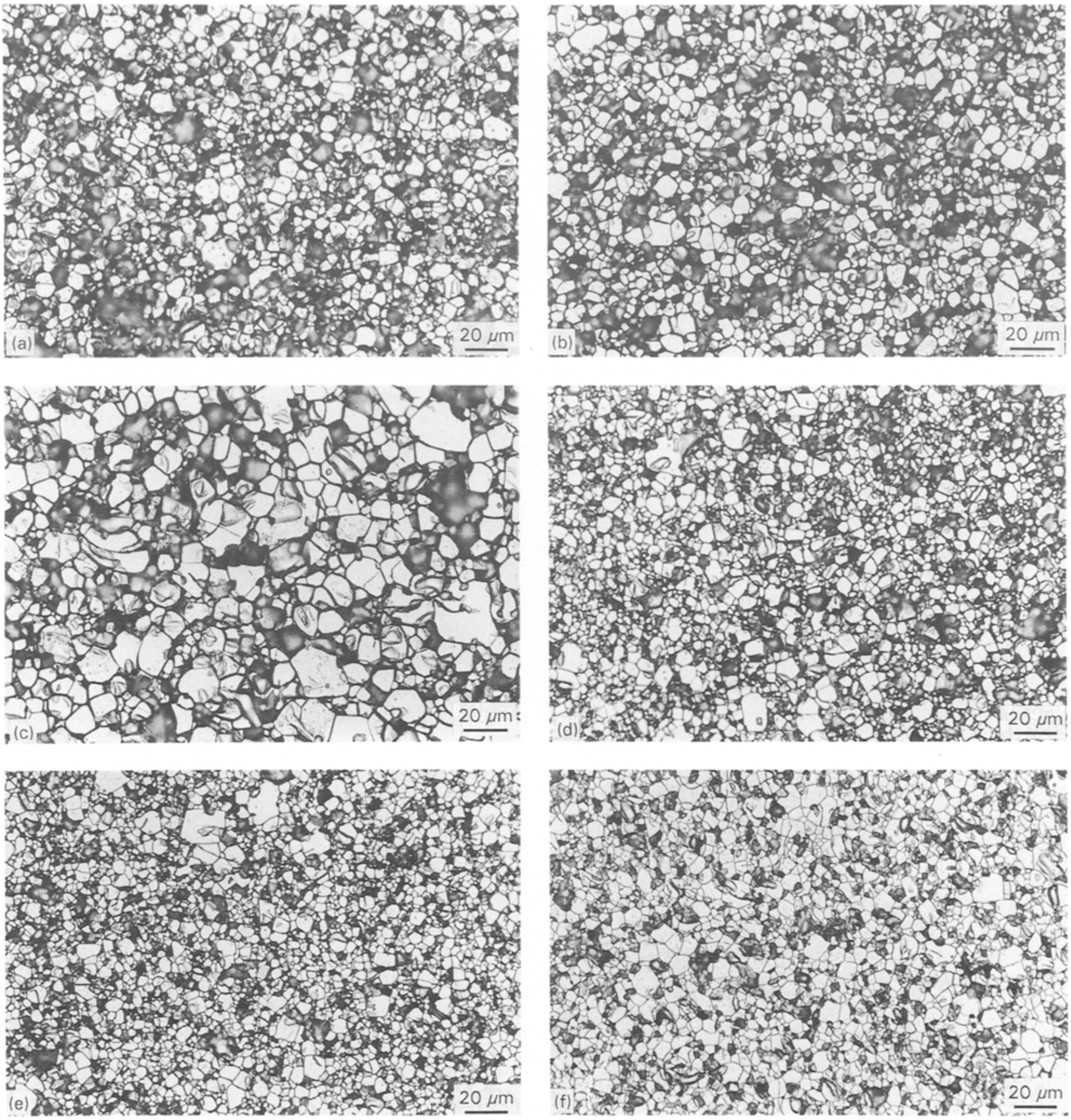

Figure 3 Optical micrographs of sintered Mn–Zn ferrite toroids prepared by injection moulding: (a) run 1 (final heating rate (FHR) 40 °C h^{-1}; sintered (S) at 1320 °C/2 h); (b) run 2 (FHR 80; S 1320 °C/2 h); (c) run 3 (FHR 80; S 1320 °C/4 h); (d) run 4 (FHR 80; S 1280 °C/2 h); (e) run 5 (FHR 80; S 1250 °C/4 h); (f) run 6 (FHR 80); 1 h hold at 1150 °C, S 1320 °C/2 h).

TABLE VI Average grain size, density and magnetic properties of injection-moulded sintered Mn–Zn ferrite toroids

Run No.	Peak temperature/ time (°C h^{-1})	MLI grain size (μm)	Density (%TD)	Initial permeability	Loss factor ($\times 10^{-6}$)
1	1320/2	5.83	89.2	1518	13.21
				1305	13.29
2	1320/2	4.80	–[a]	1238	17.34
				1360	11.71
3	1320/4	7.71	–[a]	1463	23.52
				1463	21.60
4	1280/2	4.20	87.1	922.5	24.15
				955.5	23.33
5	1250/4	4.50	90.4	717.7	37.18
6	1320/2	4.33	90.1	1609	9.10
				1456	9.61
7	1320/2	n.a.	85.1	733.4	50.94
				716.3	42.06

[a] Not available.

use of a valve to produce an oscillating pressure at the nozzle would be beneficial [15]. This procedure increases the amount of time before sprue solidification occurs.

Burning the binder out of the ferrite specimens was a major problem. For the 2 mm thick specimens, burn-out could be performed in air (although this resulted in some shrinkage of the specimens) with heating rates in the range 5–10 °C h^{-1} over the critical temperature range (150–275 °C). For the 4 mm thick specimens, a nitrogen atmosphere was required as the oxidative reaction ($\sim$ 390–425 °C) caused the surface layer to exfoliate. Binder burn-out times in both air and nitrogen were long, up to 8.5 days. The schedule used for 4 mm thick specimens should be applicable for thicker specimens; Edirisinghe [13] used such a binder burn-out schedule for step moulds with 20 mm thick sections, and for the production of ceramic rotor blades. The length of time required for burn-out is inconvenient, but should not prove prohibitive in a commercial environment as the potential benefits for the production of complicated sections are great. Complex shapes currently have to be fabricated in two or more sections and bonded together. This is a difficult process, and involves use of an adhesive to connect the sections. Injection moulding of a single component would remove the need for bonding.

Sintering of the 4 mm thick toroids employed heating rates of 40–80 °C h^{-1} (with holds) and peak temperatures of 1250–1320 °C (Table V). For ferrites, good densification is essential if satisfactory magnetic properties are to be achieved. Fired densities were typically 89–90% of the theoretical value (Table VI), falling to a minimum of 85% (run 7). The highest sintering temperature (1320 °C) generally yielded the highest densities; the heating rate and time at peak temperature had only marginal effects.

Since injection-moulded components lose significantly more material during binder burn-out, and thus have large average particle–particle separations than conventionally prepared green bodies, there is a risk that the former may exhibit lower fired densities. In fact, there is little difference between the fired densities of Mn–Zn ferrites prepared via injection moulding (Table VI) and conventionally produced specimens [12] sintered under the same conditions. The use of high-shear mixing to combine the powder and binder for injection moulding should break up agglomerates [16], leading to a reduction of defects [17] and an increase in density for such components. This almost certainly compensates for any lower initial density after binder burn-out.

For commercial applications the Mn–Zn ferrites should exhibit high initial permeability (μ) and low losses. Initial permeabilities are in the range 717–1609 (Table VI) and, in general, permeability increases with specimen density (Fig. 4). The use of a slower heating rate (40 °C h^{-1}) caused a slight increase in initial permeability and decrease in losses (see data for run 1 and run 2, Table VI), but the best properties (both μ and losses) were achieved by including a 1 h soak at 1150 °C in the sintering cycle (run 6, Table VI). Heating directly to 1320 °C and increasing the sintering period at peak temperature (run 3) led to higher losses. Specimens from run 7 should exhibit magnetic properties comparable with those from run 6, but in fact those of the former are grossly inferior. The unexpectedly low density of specimens from run 7 suggests they may have suffered internal damage prior to sintering. Although the specimens from run 5 have comparatively high densities (90.4% theoretical) the low initial permeability and high losses indicates internal defects and microstructural inhomogeneity.

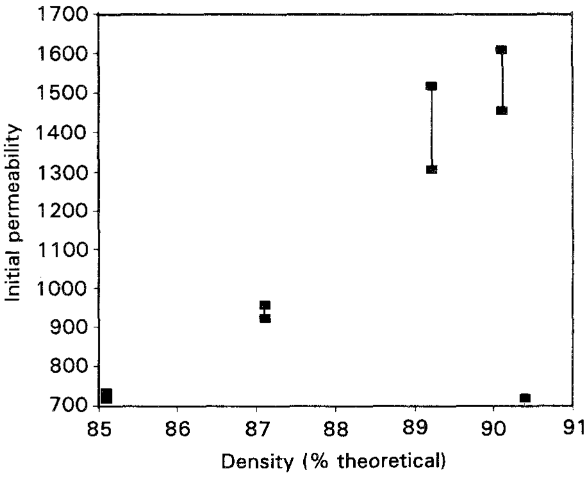

Figure 4 Initial permeability of injection-moulded ferrite toroids as a function of specimen density.

The grain sizes of the injection-moulded specimens is typically 4–6 μm (Table VI). Mn–Zn ferrite toroids prepared via a conventional spray-drying route and sintered at 1320 °C for 2 h have grain sizes of approximately 8 μm [12]. Thus the two processing routes have little effect on specimen density, but a marked effect in grain size. Longer sintering times are required for the injection-moulded specimens to achieve the same grain size as the conventionally prepared samples. Fig. 3b and c show that the grain size of injection-moulded toroids increased from 4.8 to 7.7 μm as the sintering time was increased from 2 to 4 h. The latter figure is comparable with that normally expected for Mn–Zn ferrite, but there is some evidence of exaggerated grain growth (Fig. 3c).

The magnetic properties of the toroids produced via injection moulding can only be qualitatively compared with those of conventionally produced toroids [12], as the specimen dimensions are different. Typically, conventionally produced toroids sintered under the same conditions had average initial permeabilities in the range 2000–4000. In order to improve the magnetic properties of injection-moulded specimens, the grain size needs to be increased. The smaller grain size means that there are more grain boundaries, hence more pinning centres, and hence a lower permeability. To increase initial permeability it is necessary to allow the grains additional time to grow (which may further enhance the density), whilst minimizing zinc loss through volatilization. Zinc volatilization occurs at temperatures above the boiling point of ZnO, which is 1180 °C [18]. Hence the sintering run performed with a 1 h hold at 1150 °C (run 6) produced specimens with the best magnetic properties. A temperature of 1150 °C should be high enough to encourage grain growth without zinc volatilization.

Work on Mn–Zn ferrites has shown that there is a linear relationship between average grain diameter and initial permeability (e.g. Roess [19] and Beer and Schwarz [20]), corresponding to an increase in initial permeability of approximately 700 per 1 μm increase in grain size. Considering the specimens from run 2 as an example, the grain size was 4.8 μm. Increasing this by 3 μm would give a grain size of nearly 8 μm (the average size for normal Mn–Zn ferrite processed under these conditions), and the initial permeability should increase by approximately 2100, yielding an initial permeability of ~ 3400. This figure is typical for conventionally produced Mn–Zn ferrite. Hence the low initial permeabilities of the injection-moulded specimens may be explained by the reduced grain sizes.

Further work to optimize the processing conditions, specifically the soak temperature and duration to increase the grain size and initial permeability, is now desirable.

5. Conclusions

Ceramic injection moulding can be used to produce specimens of Mn–Zn ferrite with structural integrity, densities similar to conventionally produced material, and magnetic properties which have the potential for improvement to the levels of those for conventionally produced Mn–Zn ferrite. The injection-moulded materials exhibit a high green-state strength, ideal for the fabrication of delicate and complex shapes. Although the time required for binder burn-out is long, the potential benefits, in terms of improved green strength and the production of complex shapes, makes injection moulding a very exciting processing route for the fabrication of ferrites.

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