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Powder Injection Moulding

Ceramic Injection Molding of Ni-Zn Ferrites using Thermoplastic Binder Based on PP

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Abstract

A Ceramic Injection Moulding process has been used for the manufacturing of Ni-Zn Ferrite parts. The binder was based on a combination of polypropylene and paraffin wax. Different feedstocks were prepared in order to check the effect of stearic acid. Rheology of feedstocks was evaluated using a capillary rheometer over a temperature range of 160-170-180 C and a shear-rate range of 100-3000 s^{-1}. All the feedstocks presents pseudoplastic behaviour and an important decrease of the viscosity occur when the SA is added. However, different amount of SA has not effect in this property over the shear-rate range tested. Two different debinding cycles was optimized, by means of thermogravimetric analysis. The sintering was performed at the same conditions than this type of ferrite processed by uniaxial pressure. Final densities and magnetic properties are compared with those obtained by uniaxial compacted parts.

1 INTRODUCTION

Ferrites are soft magnetic ceramic material used in plenty of electronic applications. There are three important types of commercial ferrites: Mn-Zn, Mg-Ni and Ni-Zn, more of these are processed by compaction and extrusion[1]. However, Powder Injection Moulding technology has been employed successfully for the production of Mn-Zn ferrites and it's an attractive method for the production of complex-shaped parts with thin sections cost-effectively with a high degree of precision [2,3]. This process involves blending polymeric binders with the powders to form a flowable and uniform suspension that permit to be shaped into a prescribed mould. After shaping, the polymeric binder is extracted and the powder is sintered, achieving often densities close to theoretical [4,5].

Binder compositions and debinding techniques are the main differences between various PIM operations. Most binders are multiple-component systems that contain a mayor component that dictates the basic properties with several modifiers added to suit the particular application. Recent findings have revealed the flow behaviour of the suspensions could be altered by stearic acid. This lubricant as dispersant improve the dispersion of powder in binder and as plasticizer enhances the miscibility among binder components [6,7,8,9,10].

In this work the manufacturing of Ni-Zn ferrite ceramic using the powder injection moulding process is reported. The binders used were based on a combination of polypropylene, paraffin wax and stearic acid. The composition of these binders was optimized on the basis of a rheology study. The magnetic properties of the sintered parts are discussed on the basis of density values.

2 EXPERIMENTAL PROCEDURE

2.1 Materials

The starting raw material was a granulated pre-sintered spray dried Ni-Zn Ferrite powder (FERROXCUBE), which is normally used for the industrial manufacturing of ferrites by uniaxial pressure. This powder is constituted by a mixture of Ni-Zn ferrite, Fe_2O_3, NiO and ZnO. As shown in Figure 1, the powder is heavily agglomerated (5-500 μm) in large spheres. The binder was a mixture composed by polypropylene (PP), paraffin wax (PW) and stearic acid (SA) as major ingredient, minor ingredient and lubricant, respectively.

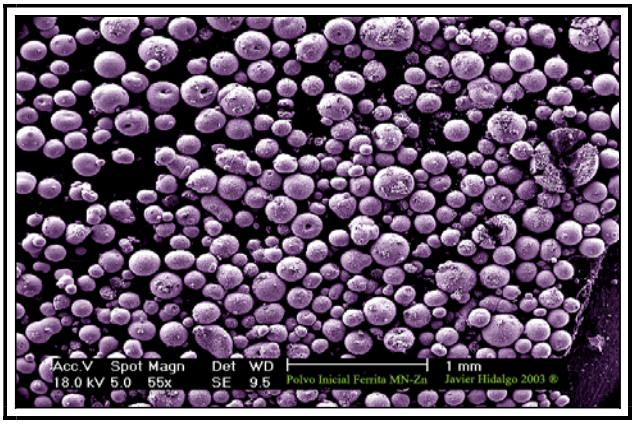

Figure 1.- Scanning electron microscopy images of Ni-Zn ferrite powder as received.

2.2 Process

Four different feedstocks (mixtures of powder and binder) were prepared according to the compositions shown in Table 1. The volume fractions of powder in the feedstock were kept at 58 %vol (88.8 %wt) while the concentrations of SA were changed from 0 to 2.9 vol% (0-0.8 %wt) by substitution of paraffin wax. Moulding step was optimized using torque measurements with a mixer machine Haake at 170 ºC and 40 rpm. In order to obtain sufficient amount of feedstock with high homogeneity degree to be injected, each component of the mixture were premixed in a Turbula mixer at room temperature during 2 hours. Then the mixtures were extruded twice in a twin screw extruder. Finally and before the injection, the mixture was pelletized.

Table 1.- Composition of mixtures in weight and volume percentage

	POWDER		PP		PW		SA	
	% vol	% wt	% vol	% wt	% vol	% wt	% vol	% wt
Feedstock 1	58,0	88,8	21,0	5,6	21,0	5,6	0,0	0,0
Feedstock 2	58,0	88,8	21,0	5,6	19,7	5,3	1,3	0,4
Feedstock 3	58,0	88,8	21,0	5,6	18,9	5,1	2,1	0,6
Feedstock 4	58,0	88,8	21,0	5,6	18,1	4,8	2,9	0,8

Rheological studies were carried out with a capillary rehometer model 8052, Galaxy V, Kayeness Inc. at 160 - 170 and 180 ºC. The die was 30,480 mm length and 1,016 mm diameter (L/D = 30). The temperatures employed were 160-170 and 180 ºC and a shear-rate range of 100-3000 s^{-1}. The moulding process was conducted by an injection machine Arburg 270 S 250-60 checking different temperatures of injection and mould which consisted in a toroid part of dimensions 17.7 x 8.7 x 4.8 mm outer diameter, inner diameter and depth respectively.

Two different debinding processes were studied: thermal and solvent-thermal debinding with the aid of a thermogravimetric analysis (TGA) using a Perkin Elmer TGA7. The carbon content of the debound specimens was determined by means of elemental analysis using a LECO instrument. Finally the toroids were sintered at the same conditions of ferrites parts obtained by uniaxial pressure (1215 ºC in air for 2 hours). The sintered densities of toroids were determined using Archimedes method. Microstructures of final specimens were examined using optical and scanning electron microscope (Philips XL30 equipped with a backscattered electron detector (BSE) and an Energy dispersive analyser (EDAX D4i)). The values of the complex magnetic permeability as a function of frequency (0-25.000 KHz) for the sintered parts were measured with a Hewlett-Packard LCR-meter HP4285A.

3 RESULTS AND DISCUSSION

3.1 Moulding

The optimization of the mixture was carried out by means of torque measurements of the different formulations prepared. Firstly, we optimized the binder composition. The binder with a 50 wt % of PP has the minor value of torque and the stabilization occur before than binders with higher PP content. Taking into account the final torque value, which indicates the lower viscosity value, we have chosen the binder with 50 % of PP to perform the feedstock. In Figure 2 torque evolution of feedstocks with 50, 55 and 58 % of powder is shown. The higher torque value was obtained for the feedstock with 58 % of powder (3.9 Nm). This result besides the viscosity curves indicates that this mixture is adequate to be injected. So we choose as base composition 58 vol % of powder in feedstock and 50-50 wt % of PP and PW as binder. To have enough mixture to be injected, the feesdock was prepared in a twin screw extruder**.** In order to study the effect of stearic acid in the properties of the mixtures we added 3, 5 and 7 wt% in binder.

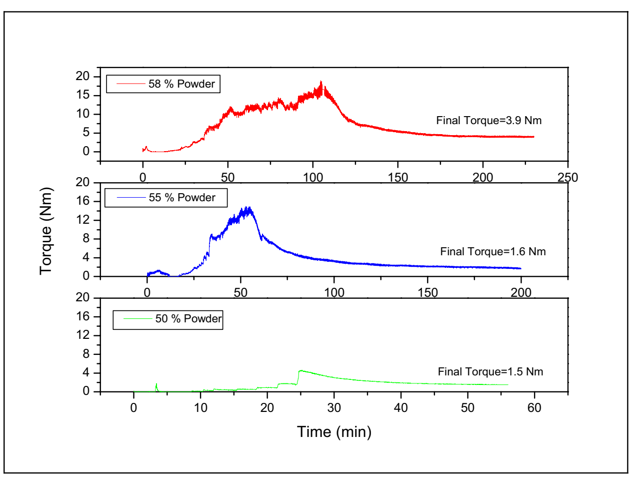

Figure 2.- Torque evolution of feedstocks with 50, 55 and 58 % of powder

Figure 3 shows the viscosity of the four feedstocks. We see that all the mixtures are homogeneous and the viscosity is lower when we added stearic acid but it is independent of the amount of this agent. The result was the same in the case of 160 and 180 ºC.

The injection process for the four feedstock was carried out at eight different temperatures, from 170 to 205 ºC with increments of 5 ºC finding the same results of green density in all case (3.3 g/cm^3, 96 % th). The mould optimum temperature was 40 ºC because for higher temperatures flux and ejector signals appeared and lower temperatures caused cracks at first sight.

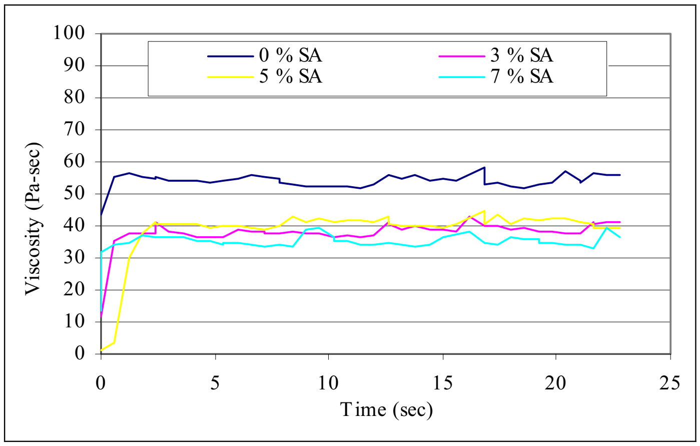

Figure 3.- Viscosity of the four feedstocks at a shear rate of 1500 s^{-1} at 170 ºC

3.2 Debinding process

Different debinding cycles were designed by means of thermogravimetic analysis of all components of binder and two binders with and without SA (Figure 4). The range of temperatures is wider and the decomposition is more gradual when SA was added in the binder. Table 2 shows the range temperatures and total times of cycles tested and %C values of the parts after debinding cycles.

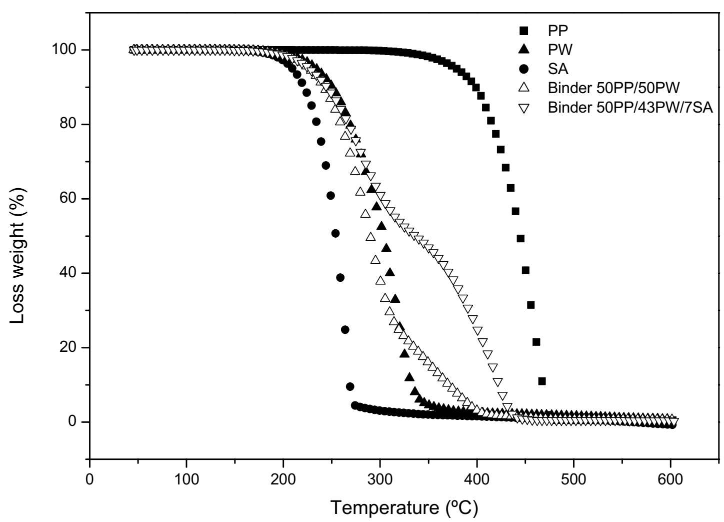

Figure 4.- TGA of components of binder and binder with and without SA

Table 2.- Debinding cycles tested, total times and %C

Cycle	Rate 1 (0-200 ºC)	Holding 1 (200 ºC)	Rate 2 (200-400ºC)	Holding 2 (400 ºC)	Total time (h)	%C
DPS	Solvent debinding		n-heptano, 60 ºC, 2 hours		2 + 8,7	0,0179
	5 ºC / min	1 hour	1 ºC / min	2 hours		
D1	5 ºC / min	1 hour	1 ºC / min	2 hours	8,7	0,0158
D2	1 ºC / min	1 hour	0,5 ºC / min	2 hours	13,0	0,0155
D3	1 ºC / min	1 hour	0,25 ºC / min	2 hours	19,7	0,0213
D4	0,5 ºC / min	1 hour	0,25 ºC / min	2 hours	23,0	0,0172

The first cycle was developed with a rate of 5 ºC/min in the first step (rate 1) and 1 ºC/min for the second one (rate 2). We checked than the toroids obtained had a large number of defects like bubbles and cracks after this first cycle. So, next cycles were performed reducing the heating rates. Using debinding D2 and D3 few parts have good appearance. The optimized cycle was D4 because the parts have not defects. We tested the use of alumina powder to try wick debinding, but it was very difficult to remove it before sintering process and it caused grain growth in final parts. As the D4 cycle need too much time (23 hours) we designed a solvent-thermal debinding (DPS cycle) in order to reduce it. Paraffin wax is soluble in n-heptane; this fact allows using this solvent to remove this component. Figure 5 shows the time necessary for the total elimination of PW at 60 ºC. In this cycle DPS, the parts had not defects for all the compositions. In all cycles employed the organic components were totally removed as confirm the LECO analysis (Table 2).

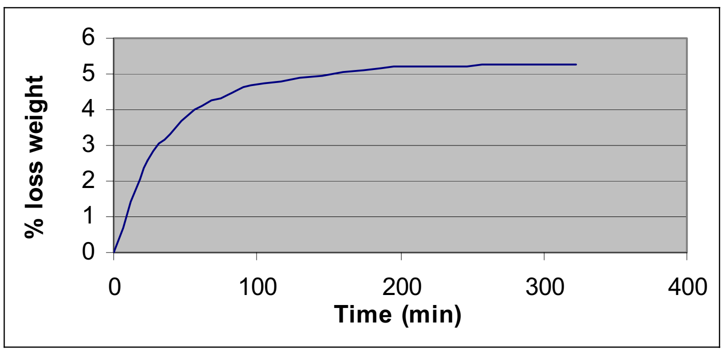

Figure 5.- Loss weight of solvent debinding in n-heptane of 7% SA samples at 60 ºC

3.3 Sintering and final properties

The sintering process was exactly the same used for the industrial sintering of uniaxial compacted samples of this ferrite. By means of XRD and SEM experiments the single phase of ferrite, after sintering, was confirmed. Table 3 shows density and permeability of the two types of debinding performed both PIM final parts and uniaxial pressure processed toroids. The densities achieved were near to 90 % of theoretical densities and higher than uniaxial pressure values. The permeability is similar to the parts obtained by uniaxial pressure (340.000) at of 100 KHz. There is a correlation between permeability and density. It is clear to found a relationship between the permeability and time of thermal debinding. For the same density values we observed that lower permeability values were obtained for longer debinding times. It could be explained because longer thermal cycle produces zinc losses and falls the permeability.

Table 3.- Density and permeability of sintered toroids

Debinding	μi (100 KHz)	Density	% Th
D4	276.140	4,71	86,87
D4	297.380	4,80	88,52
D4	301.895	4,94	91,10
DPS	343.294	4,67	86,22
DPS	366.190	4,73	87,26
DPS	384.745	4,83	89,09
Uniaxial pressure	340.000	4,82	88,93

4 CONCLUSIONS

The main conclusions deduced from this experimental work are:

Ni-Zn ferrites parts have been obtained by Powder Injection Moulding using a binder based on PP.

The stearic acid reduces the viscosity from 60 to 40 Pas.sec, however different amount of SA has not important effects in this property in the shear-rate range tested. Take into account the decrease of viscosity it would be possible to increase the powder loading.

The debinding process has been optimized. As the time necessary is too long we also optimized a solvent + thermal debinding reducing from 23 to 11 hours.

The final densities achieve were a little bigger than those obtained by uniaxial pressure and the permeabilities are in the same range.

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