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FERRITES: PART V.

A PRELIMINARY INVESTIGATION OF THE EFFECTS OF SOME OPERATIONAL VARIABLES ON THE PROPERTIES OF Mn-Zn FERRITES

by

Sutarno, W.S. Bowman and G.E. Alexander

Mineral Sciences Division

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SUMMARY

A preliminary investigation of the effects of some operational variables on the properties of Mn-Zn ferrites has been conducted. It was found that changing calcination temperature from 900 to 1000°C, milling time from 24 to 48 hr, and forming pressure from 5,000 to 10,000 psi had significant but small effects on the green density of Mn-Zn ferrites. The above variables, together with changes in the sintering temperature from 1250 to 1300°C and in the soaking time from 120 to 240 min had an effect on the oxygen stoichiometry of the final products, whereas the effect of changing the sintering atmosphere from (99.5 vol % N_2 + 0.5 vol % O_2) to (96.0 vol % N_2 + 4.0 vol % O_2) was insignificant.

The permeability of the final product was found to vary from 6 to 1208, and the Q factor varied from 9 to 5421 at 10 kHz for different combinations of variables.

The raw materials used for this series of experiments all originated from the same batch of mixed oxides.

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INTRODUCTION

The electronic properties of Mn-Zn ferrites depend not only on their intrinsic properties but also on the ceramic properties of the pieces. Most of the earlier work on the ceramic properties of this material related to the effects of various sintering variables such as temperature, time, and atmosphere on the final properties of the pieces. Much less effort has been devoted to the study of the effects of preparation variables before sintering. Experience with hexagonal ferrites has shown that these pre-sintering variables such as milling time, calcination temperature, and forming pressure had some effects on the ceramic and magnetic properties of the products[1,2,3]. It seems reasonable to suppose that the same might be true for the spinel ferrites.

This work was intended to survey, semi-quantitatively, the effects of these operational variables on the final properties of the sintered Mn-Zn ferrite pieces. A complete 2^N-factorial design was used for this purpose[4]. The following six variables: calcination temperature, milling time, forming pressure, sintering temperature, soaking time, and sintering atmosphere were investigated. The starting composition was constant (i.e., taken from the same batches of raw materials).

EXPERIMENTAL

(a) Experimental Scheme

The general experimental procedure is illustrated in the schematic diagram in Figure 1.

There are six variables (factors) to be determined. A complete 2^N-factorial design was used. Sixty-four samples would be required to cover all possible factor combinations. It was, however, considered

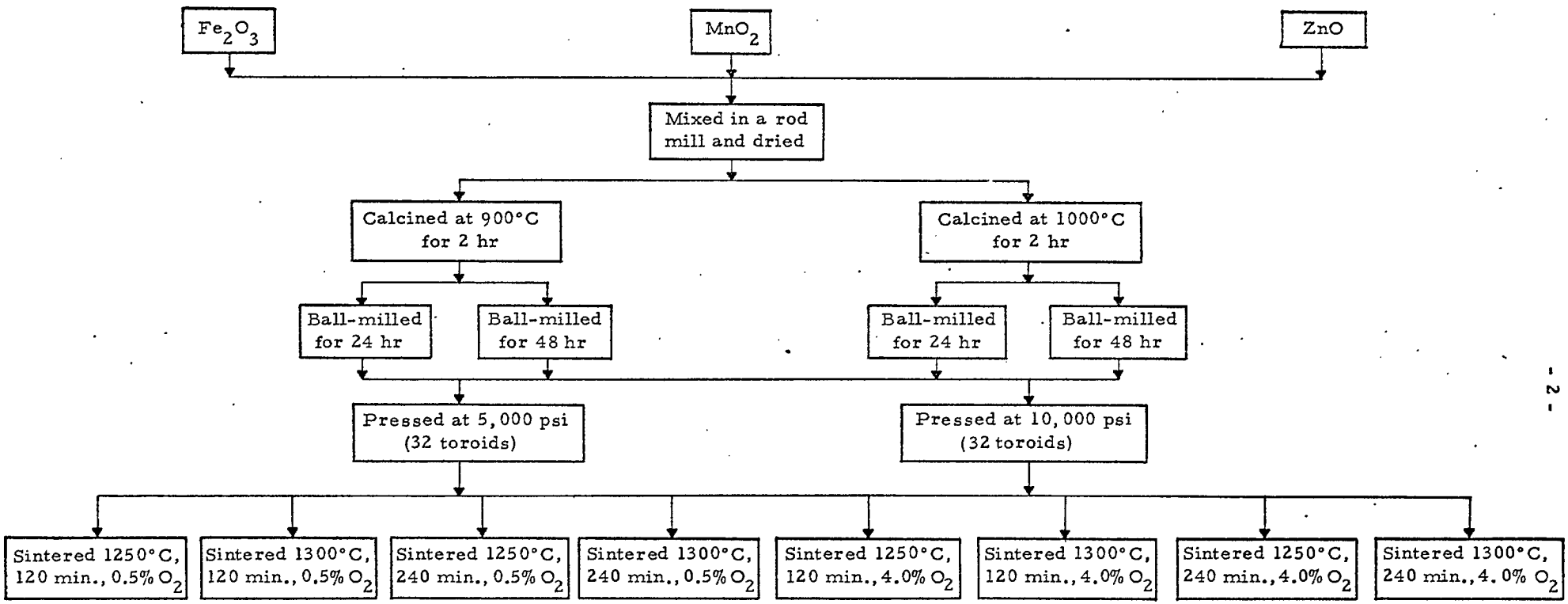

Figure 1. Schematic Diagram of the Preparation of Mn-Zn Ferrite.

impractical to prepare all sixty-four independent samples. For this reason, various factors were combined during the preparation. The design matrix for this experiment is illustrated in Table 1. Only one specimen was prepared for each combination of factors.

Schematically, the preparation of these samples consisted of the following operations:

1. mixing of all raw materials into one batch;
2. two calcinations, one at 900°C and the other at 1000°C, for 16 hr;
3. four ball-millings; two for 24 hr, and two for 48 hr;
4. sixty-four fabrications; thirty-two at a forming pressure of 5,000 psi and thirty-two at a forming pressure of 10,000 psi;
5. eight sintering combinations of sintering temperatures of 1250 and 1300°C, soaking times of 120 and 240 minutes, and sintering atmospheres of (99.5 vol % N_2 + 0.5 vol % O_2) and (96.0 vol % N_2 + 4.0 vol % O_2)

(b) Detailed Experimental Procedure

The materials used for this series of experiments were reagent-grade Fe_2O_3, MnO_2, and ZnO. No pre-purification was conducted with these materials.

2440.0 g of Fe_2O_3, 647.3 g of MnO_2, and 541.6 g of ZnO were mixed in a rod mill for 16 hr. The liquid used with this charge was 6.5 litres of ethanol. The mass was then filtered and dried at 110°C. The intended final composition was $Mn^{+2}_{0.500}Zn^{+2}_{0.447}Fe^{+2}_{0.053}Fe^{+3}_{2}O_4$.

This powder mixture was then divided into two equal parts. The first portion was calcined in air at 900°C; the second portion was calcined in air at 1000°C, both for 2 hr. The calcinations were performed in a tube furnace, and the temperature was controlled to within $\pm$ 5°C.

Each portion of the calcined powder was then divided into two parts. The first part of each portion was ball-milled for 24 hr and the second for 48 hr. The liquid used with this charge was 2 litres of ethanol. The masses were then dried in air at 110°C.

TABLE 1

Experimental Scheme for the Study of Mn-Zn Ferrite

Sample No.	Factor A	B	C	D	E	F	Sample No.	Factor A	B	C	D	E	F
1	-1	-1	-1	-1	-1	-1	33	-1	-1	-1	-1	-1	1
2	1	-1	-1	-1	-1	-1	34	1	-1	-1	-1	-1	1
3	-1	1	-1	-1	-1	-1	35	-1	1	-1	-1	-1	1
4	1	1	-1	-1	-1	-1	36	1	1	-1	-1	-1	1
5	-1	-1	1	-1	-1	-1	37	-1	-1	1	-1	-1	1
6	1	-1	1	-1	-1	-1	38	1	-1	1	-1	-1	1
7	-1	1	1	-1	-1	-1	39	-1	1	1	-1	-1	1
8	1	1	1	-1	-1	-1	40	1	1	1	-1	-1	1
9	-1	-1	-1	1	-1	-1	41	-1	-1	-1	1	-1	1
10	1	-1	-1	1	-1	-1	42	1	-1	-1	1	-1	1
11	-1	1	-1	1	-1	-1	43	-1	1	-1	1	-1	1
12	1	1	-1	1	-1	-1	44	1	1	-1	1	-1	1
13	-1	-1	1	1	-1	-1	45	-1	-1	1	1	-1	1
14	1	-1	1	1	-1	-1	46	1	-1	1	1	-1	1
15	-1	1	1	1	-1	-1	47	-1	1	1	1	-1	1
16	1	1	1	1	-1	-1	48	1	1	1	1	-1	1
17	-1	-1	-1	-1	1	-1	49	-1	-1	-1	-1	1	1
18	1	-1	-1	-1	1	-1	50	1	-1	-1	-1	1	1
19	-1	1	-1	-1	1	-1	51	-1	1	-1	-1	1	1
20	1	1	-1	-1	1	-1	52	1	1	-1	-1	1	1
21	-1	-1	1	-1	1	-1	53	-1	-1	1	-1	1	1
22	1	-1	1	-1	1	-1	54	1	-1	1	-1	1	1
23	-1	1	1	-1	1	-1	55	-1	1	1	-1	1	1
24	1	1	1	-1	1	-1	56	1	1	1	-1	1	1
25	-1	-1	-1	1	1	-1	57	-1	-1	-1	1	1	1
26	1	-1	-1	1	1	-1	58	1	-1	-1	1	1	1
27	-1	1	-1	1	1	-1	59	-1	1	-1	1	1	1
28	1	1	-1	1	1	-1	60	1	1	-1	1	1	1
29	-1	-1	1	1	1	-1	61	-1	-1	1	1	1	1
30	1	-1	1	1	1	-1	62	1	-1	1	1	1	1
31	-1	1	1	1	1	-1	63	-1	1	1	1	1	1
32	1	1	1	1	1	-1	64	1	1	1	1	1	1

Factors are:

A Calcination temperature, 900°C or 1000°C,
B Milling time, 24 hr or 48 hr,
C Forming pressure, 5,000 psi or 10,000 psi,
D Sintering temperature, 1250°C or 1300°C,
E Soaking time, 120 min or 240 min,
F Sintering atmosphere, (99.5% N_2 + 0.5% O_2) or (96% N_2 + 4.0% O_2).

Batches, approximately 15 g, of the calcined, milled powder were pressed in the form of toroids having 1.5-inch OD and 0.75-inch ID. The forming pressures used were 5,000 and 10,000 psi. Sixty-four toroids were fabricated. The green density of the toroids was measured by the geometric method.

The toroids were then sintered in a tube furnace in batches of eight. The heating rate was 75 deg C per hr. The sintering temperatures used were 1250 and 1300°C, controlled to within $\pm$ 3°C. The soaking times used were 120 and 240 minutes and the sintering atmospheres were (99.5 vol % N_2 + 0.5 vol % O_2) and (96.0 vol % N_2 and 4.0 vol % O_2). The oxygen concentrations in the atmospheres used during sintering were the supplier's specifications for the particular gas supplies.

RESULTS AND DISCUSSION

There were six factors to be investigated simultaneously. For convenience, these factors were arranged in the following manner.

Factor No.	Controlled Variables	Low Value (-1)	High Value (+1)	One Coded Unit Equivalent to
A	Calcination temperature	900°C	1000°C	50 deg C
B	Milling time	24 hr	48 hr	12 hr
C	Forming pressure	5,000 psi	10,000 psi	2,500 psi
D	Sintering temperature	1250°C	1300°C	25 deg C
E	Soaking time	120 min.	240 min.	60 min.
F	Percentage oxygen in sintering atmosphere	0.50%	4.00%	1.75%

(a) Green Density

Only three factors, viz., A, B, and C, will have any effect on the green density. Sixty-four specimens were prepared; so there were eight replicate measurements available for each factor combination. The results of these measurements are listed in Table 2. The following model was used as the starting model to analyse these results:

$$Y_i = K_0 + K_1A + K_2B + K_3AB + K_4C + K_5AC + K_6BC + K_7ABC \quad \ldots \text{(Eq. 1)}$$

where

Y_i = the green density of Mn-Zn ferrite at factor combination i;

i = 1, 2 ..., 8;

K's = parameters to be determined;

A, B, and C = values of factors in coded units.

The regression coefficients and their corresponding sums of squares (which are equal to their mean square in this case, because they have a degree of freedom of 1) are listed in Table 3. The residual error in this case (σ^2) was computed from the pool of errors of all experimental points and carries a degree of freedom of 56; it was found to be 0.000954. The standard deviation, σ, which was found to be 0.030 g/cm^3, is reasonably good for a green-density measurement. By comparing the ratio of the mean squares to the mean square error (σ^2) with the F-distribution value[5], it was found that K_0, K_1, K_2, K_3, and K_4 are significant to better than the 99.99% level. K_5 and K_7 are insignificant and K_6 is significant only at the 95% level and insignificant at the 97.5% level.

The model was then simplified as follows:

$$Y_i = = K_0 + K_1A + K_2B + K_3AB + K_4C \quad \ldots \text{(Eq. 2)}$$

and the computation was repeated. The result of the second computation showed that the coefficients (K's) remained constant and that the error, σ^2, increased only slightly to 0.000999 (or σ = 0.032). The linear model

TABLE 2

Green Density of Mn-Zn Ferrites at Various Factor Combinations

Factor			Green Density in g/cm^3							
A	B	C	#1	#2	#3	#4	#5	#6	#7	#8
-1	-1	-1	2.4933	2.6355	2.5555	2.6387	2.5435	2.6343	2.6288	2.6419
1	-1	-1	2.6614	2.6374	2.6354	2.6413	2.6569	2.6233	2.6744	2.6977
-1	1	-1	2.4338	2.4352	2.4388	2.4367	2.4126	2.4158	2.4409	2.4128
1	1	-1	2.5959	2.6081	2.5451	2.6075	2.5807	2.5985	2.6199	2.5958
-1	-1	1	2.7621	2.8039	2.7624	2.7532	2.7564	2.7446	2.6921	2.7719
1	-1	1	2.8294	2.8029	2.8678	2.8346	2.8384	2.8587	2.7776	2.8181
-1	1	1	2.6883	2.6353	2.6181	2.6155	2.6353	2.6284	2.6421	2.6253
1	1	1	2.8048	2.7658	2.7830	2.8406	2.7721	2.7660	2.7709	2.8115

TABLE 3

Regression Coefficients and Their Corresponding Mean Squares for the Green Density of Mn-Zn Ferrites as a Function of the Operational Variables

Factor	Coefficient		Mean Squares M_s	M_s/σ^2	Remarks
Const.	K_0	2.660227	452.915543		Significant
A	K_1	0.056070	0.201208	210.91	Significant
B	K_2	-0.048317	0.149411	156.62	Significant
AB	K_3	0.023658	0.035820	37.04	Significant
C	K_4	0.092183	0.543851	570.07	Significant
AC	K_5	0.000408	0.000011	0.01	Insignificant
BC	K_6	0.008595	0.004728	4.96	Significant
ABC	K_7	-0.003486	0.000778	0.82	Insignificant
Error (σ^2)			0.000954		

of green density of Mn-Zn ferrite of this composition can, therefore, be expressed as:

$$Y = 2.660 + 0.056A - 0.048B + 0.024AB + 0.092C \quad \ldots \text{(Eq.3)}$$

If A is expressed in deg C, B in hr, and C in psi units, Equation 3 becomes:

$$Y = 2.66 + [(112A - 403B + 4AB + 4C) \times 10^{-5}] \quad \ldots \text{Eq.4)}$$

If the laboratory equipment can provide a control of temperature to within $\pm$ 5°C, of forming pressure to within $\pm$ 100 psi, and of milling time to within $\pm$ 1 hr, then, using the same raw materials and composition throughout, the green density should be reproducible to within $\pm$ 0.01.

(b) Weight Loss during Sintering

The weight losses during sintering were measured and the results are listed in Table 4. The results were analysed by a full 2^6-factorial method. As no replicate measurements were available, so the high-order interactions, i.e., the interactions of three or more factors, excepting ABD interactions, were considered as being insignificant. Their sums of squares were then pooled, to be considered as the measurement error sum of squares and to be used for further eliminations of insignificant factors. The resulting significant factors are listed in Table 5. The measurement error, expressed as the coefficient of variation of the weight loss, was found to be 9.4%.

The results of this analysis show that the weight loss during sintering is independent of the sintering atmosphere at the oxygen levels used. As would be expected, the weight loss was affected by the calcination and sintering temperatures and, to a smaller extent, by the soaking time. Rather unexpectedly, however, the weight loss was affected also by the variation in milling times.

There are two possible explanations of the effect of milling time on the weight loss during sintering. The first possibility is that the materials picked up iron in the form of Fe_2O_3 from the balls. However, this is unlikely

TABLE 4

Weight Loss of Mn-Zn Ferrites During Sintering

Sample No.	Weight loss,%	Sample No.	Weight loss,%	Sample No.	Weight loss,%	Sample No.	Weight loss,%
1	1.19	17	1.43	33	1.17	49	1.37
2	0.03	18	0.47	34	0.27	50	0.19
3	1.94	19	1.94	35	1.93	51	1.91
4	1.20	20	1.19	36	1.02	52	1.16
5	1.56	21	1.52	37	1.53	53	1.45
6	0.64	22	1.06	38	0.37	54	0.60
7	1.95	23	1.91	39	1.91	55	1.89
8	1.18	24	1.23	40	1.07	56	1.11
9	1.56	25	1.58	41	1.52	57	1.62
10	0.75	26	1.25	42	0.92	58	1.22
11	1.98	27	1.99	43	1.96	59	1.96
12	1.18	28	1.27	44	1.23	60	1.25
13	1.51	29	1.60	45	1.53	61	1.58
14	1.17	30	1.23	46	1.24	62	1.21
15	1.94	31	1.96	47	1.94	63	1.94
16	1.22	32	1.22	48	1.27	64	1.19

TABLE 5

Regression Coefficients and Sums of Squares of the Weight Loss of the Mn-Zn Ferrites as a Function of the Operational Variables

Factor	Coefficient	Sums of Squares	Operational Variable
A	-0.363	8.424506	Calcination temperature
B	0.213	2.907025	Milling time
C	0.049	0.154056	Forming pressure
BC	-0.054	0.191406	
D	0.120	0.916806	Sintering temperature
AD	0.069	0.302500	
BD	-0.090	0.514806	
CD	-0.031	0.062500	
ABD	-0.057	0.207025	
E	0.040	0.102400	Soaking time
BE	-0.034	0.072900	
Constant	1.351	116.748025	

because of the fact that ethanol was used as the slurry liquid; also, the balls were thoroughly cleaned. The second possibility is that the reaction was incomplete and the unreacted hematite particles were coated by the reaction product. Thus, by milling, these hematite particles were exposed and the reactions could proceed faster.

The raw materials contain 42.27 wt % of oxygen, based on the total weight of the metals content. The completely-reacted product would contain 37.35 wt % of oxygen on the same basis. The theoretical weight loss during reaction should be 4.92 wt %. The oxygen partial pressure in the formation of Fe_3O_4 from Fe_2O_3 was estimated to be 1.6×10^{-7} atm, and that in the reduction of MnO_2 to MnO was 1.7×10^{-1} atm[6]. Therefore, there would not be any reduction of Fe_2O_3 until the supply of MnO_2 has been exhausted. If there would be no further reduction of Fe_2O_3 beyond the formation of the spinel, Fe_3O_4, the amount of Fe^{2+} would be 0.053 gram-atom per mole of spinel. This would correspond to the liberation of 0.42 gram O_2 per mole of ferrite. Because the average weight loss is 1.35% of the original weight, which is much more than can be attributed to the unreduced Fe_2O_3, the final products (toroids) must exhibit some variation in composition.

If it can be assumed that, in the calcined state, the powders had achieved the same degree of reaction, i.e., that the powder was homogeneous throughout the batch for a given calcination temperature, then the variation in the oxygen content of the final product can be estimated. The average weight loss of the samples prepared from the powder calcined at 900°C was found to be 1.71% with a standard deviation of 0.25%; the average weight loss of the samples calcined at 1000°C was found to be 0.99% with a standard deviation of 0.36%. These variations in oxygen content of the samples, which were caused by the different values of the operational variables, would probably cause differences in both the ceramic and electronic properties of the final products.

(c). Electronic Properties

The results of the sintering experiments were disappointing. Twenty out of sixty-four samples were cracked during sintering. The remaining samples were lapped into perfect toroids and their electronic properties were measured. The results are listed in Table 6 in the form of permeability and Q factor measurements. Reliable density measurements could not be made because of the possible presence of internal hair-line cracks. Density measurements by the immersion method produced densities that varied from sample to sample, from 4.73 g/cm^3 for Sample No. 6 to 4.97 g/cm^3 for Sample No. 2. This method of density measurement, however, is not considered reliable because the values obtained are far below the known X-ray density of this material ($\approx$ 5.2 g/cm^3).

Because of the number of missing samples, a meaningful factorial analysis was not possible. However, Table 6 shows that changes in the combination of these variables can completely alter the electronic properties of the samples, although they were all prepared from the same batch. The permeability varies from virtually zero for Sample No. 18 to about 1208 for Sample No. 9. It is also seen in Table 6 that the permeability is virtually independent of the frequency. The coefficients of variation were generally below 5% for the frequency used, except for those samples with very low permeability. The Q factor, however, seems to vary both from sample to sample and also with the measurement frequency.

TABLE 6

Electronic Properties of Mn-Zn Ferrites at Various Combinations of Operational Variables

Sample No.	Permeability, μ				Q		
	10 kHz	100 kHz	500 kHz	CV.%*	10 kHz	100 kHz	500 kHz
1	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-
5	1008	1031	1049	2.0	950	205	48
6	-	-	-	-	-	-	-
7	766	766	780	1.1	716	154	32
8	-	-	-	-	-	-	-
9	1208	1141	1170	2.8	250	90	28
10	23	26	25	5.9	14	40	27
11	760	785	814	3.4	445	86	14
12	952	965	969	0.9	596	201	37
13	858	881	897	2.2	230	128	26
14	652	643	652	0.8	406	146	46
15	758	756	787	2.3	358	120	19
16	810	807	892	5.8	1518	112	18
17	289	285	294	1.6	5421	153	81
18	6	6	6	5.2	9	15	7
19	-	-	-	-	-	-	-
20	834	837	850	1.0	1571	145	35
21	-	-	-	-	-	-	-
22	149	152	152	1.4	279	150	84
23	559	565	576	1.5	351	123	25
24	789	790	832	3.1	742	82	14
25	908	901	922	1.2	337	145	33
26	1161	1187	1199	1.6	337	122	38
27	-	-	-	-	-	-	-
28	847	835	896	3.8	159	60	9
29	-	-	-	-	-	-	-
30	793	779	780	1.0	247	175	58
31	-	-	-	-	-	-	-
32	-	-	-	-	-	-	-
33	33	31	31	3.9	61	51	36
34	-	-	-	-	-	-	-

(continued on page 13)

TABLE 6 continued -

Sample No.	Permeability μ				Q		
	10 kHz	100 kHz	500 kHz	CV %*	10 kHz	100 kHz	500 kHz
35	-	-	-	-	-	-	-
36	-	-	-	-	-	-	-
37	1043	1041	1057	0.9	218	180	43
38	-	-	-	-	-	-	-
39	811	811	820	0.7	506	202	45
40	540	539	541	0.2	253	259	92
41	-	-	-	-	-	-	-
42	54	48	51	5.8	49	87	50
43	-	-	-	-	-	-	-
44	886	880	900	1.2	897	175	34
45	820	872	886	4.1	765	199	54
46	975	975	997	1.3	901	180	45
47	783	782	820	2.7	291	104	16
48	799	818	863	4.0	166	75	12
49	760	759	767	0.6	478	167	48
50	-	-	-	-	-	-	-
51	838	839	860	1.5	732	131	25
52	900	896	908	0.7	559	169	41
53	504	506	510	0.6	722	234	66
54	-	-	-	-	-	-	-
55	516	516	527	1.2	161	121	25
56	404	403	405	0.2	757	252	96
57	881	887	927	2.8	825	111	19
58	1028	1025	1050	1.3	387	172	42
59	759	725	757	2.5	651	97	16
60	790	792	848	4.1	491	73	11
61	722	724	749	2.1	449	126	24
62	762	755	766	0.7	238	217	60
63	745	720	754	2.4	462	86	14
64	467	470	483	1.8	292	124	24

NOTE: Where no result is shown, the specimen was cracked or broken and could not be measured.

*CV % Coefficient of variation is the standard deviation expressed in terms of percentage of the mean.

CONCLUSIONS

From these preliminary experiments, the following conclusions can be drawn:

(1) Given a constant group of raw materials, the green density of Mn-Zn ferrite can easily be controlled to within $\pm$ 0.01 g/cm^3. The effects on the green density of variations in the properties of the raw materials could then be investigated.

(2) The weight loss during sintering and, therefore, the completion of the formation reaction of the Mn-Zn ferrite are not only affected by the heat-associated operational variables (calcination temperature, sintering temperature, and soaking time) but are also affected by the milling time, presumably via the particle size of the raw materials or through an intermediate product.

(3) The permeability of the specimens prepared varies very strongly with the different combinations of operational variables but is independent of the measuring frequency. The Q factor, however, decreases with the increase of the measuring frequency.

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