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MINERAL SCIENCES DIVISION

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The effects of sintering atmosphere on the properties of strontium ferrite permanent magnets

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

ABSTRACT. The effects of variations in the partial pressure of oxygen in the sintering atmosphere on the ceramic and magnetic properties of strontium ferrite ceramic magnets have been investigated. It was found that, at given sintering parameters (i.e. temperature, time, heating rate, etc.), the increase of oxygen partial pressure reduced the degree of sintering, and consequently decreased the remanent magnetization and increased the coercive force.

Introduction

The process used to manufacture a ferrite permanent magnet is basically similar to those used to manufacture other ceramic pieces. It consists mainly of mixing the raw materials in prescribed proportions, with each raw material being introduced into the mixture at a given stage of the process, reacting them to form a hexaferrite powder, comminuting this powder to a suitable particle size for further fabrication stages, fabricating the pieces, sintering them and finishing the product to the desired geometry.

Even assuming that one is able to obtain sources of suitable raw materials having acceptable reproducibility, the complexity of the process can still produce a wide variation in the quality of the finished products. In order to be able to apply adequate process control to yield products with an acceptable quality-tolerance required for a particular application, the sensitivity to each of the process variables should be known. Some of the effects of these process variables, mainly the calcination temperature and time, the milling time, the forming pressure, the sintering time and temperature, have been previously studied and reported.[1,2] The purpose of the present work is to investigate the effect of sintering atmosphere on the ceramic and magnetic properties of strontium ferrite permanent magnets. Strontium ferrite was chosen because of its superior properties, by comparison with those of either its barium or lead counterparts.[3]

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Experimental procedures

In order to avoid the problem of non-reproducibility of the raw materials, the ferrite powders used in this work were from the same batches as those used in previous work.[2] The raw materials were reagent-grade strontium carbonate and iron oxide (Fe_2O_3) powders. The spectrographic analyses of these powders are listed in Table I.

The experimental procedure is illustrated schematically in Figure 1. For each of three batches, five pounds of iron oxide powder were mixed with the appropriate amount of strontium carbonate to yield the nominal composition $SrO.5 \cdot 5Fe_2O_3$. The mixing was done in a rod mill, using an alcohol medium in place of water, to guard against possible strontium losses by solution. After batch calcinations at 900° and 1100°C, the masses were ball-milled in an 8 in.-diameter steel mill using 3/8 in.-diameter steel balls. The mass ratio of ferrite:alcohol:balls was 1:4:35.

Discs, 1.5 in. in diameter, were pressed under a magnetic field of approximately 13,000 oersted from

*Table I. Semi-quantitative spectrographic analysis of raw materials and of the nominal $SrO.5{\cdot}5Fe_2O_3$ (Wt. %)**

Elements	$SrCO_3$	Fe_2O_3	Strontium ferrite (nominal) Batch No. 1	Batch No. 2	Batch No. 3
Ba	–	ND	ND	ND	ND
B	ND	–	ND	ND	ND
Mn	ND	0.06	0.02	0.02	0.02
Sb	ND	ND	ND	ND	ND
Mg	ND	0.04	0.01	0.01	0.01
As	ND	–	ND	ND	ND
Mo	ND	ND	ND	ND	ND
W	ND	ND	ND	ND	ND
Pb	ND	ND	ND	ND	ND
Sn	ND	ND	ND	ND	ND
Cr	ND	ND	0.03	0.03	0.03
Si	0.03	0.03	ND	ND	ND
Nb	ND	–	ND	ND	ND
Ta	ND	–	ND	ND	ND
Fe	ND	PC	PC	PC	PC
Ge	ND	–	ND	ND	ND
Bi	ND	ND	ND	ND	ND
Al	ND	0.006	0.01	0.04	0.02
In	ND	–	ND	ND	ND
Zr	ND	ND	ND	ND	ND
Cu	ND	0.01	ND	ND	ND
Ag	ND	ND	ND	ND	ND
Na	ND	ND	ND	ND	ND
Zn	ND	ND	ND	ND	ND
Ti	ND	ND	ND	ND	ND
Ni	ND	0.03	ND	ND	ND
Co	ND	ND	ND	ND	ND
Sr	PC	ND	PC	PC	PC
Ca	0.07	–	ND	ND	ND

*ND – Non-detectable; PC – Principal constituent.

the ferrite slurries.[4] The forming pressure, which was read on a calibrated hydrostatic pressure gauge, was 5000 psi. The compacts were demagnetized by heating them to 500°C in order to facilitate handling and measurement of "green" density.

The discs were sintered in an electrically-heated tube furnace at 1160°C, at 1180°C or at 1200°C. The heating rate was 100°C per hour and the soaking time was 120 minutes. The sintering atmospheres were nitrogen (containing about 0.01% oxygen), a mixture of 4% (by volume) oxygen and 96% nitrogen, air (which contains 20.95% oxygen), and pure oxygen. The gas flow-rate was kept constant and the specimens were arranged in the furnace in the same way for each run, so that the effective gas flow-rate with respect to the specimens remained constant. A static-air atmosphere was also employed. The specimens were cooled in the same atmosphere at the natural cooling rate of the furnace. The discs were lapped to cylinders with their faces parallel to within 0.0002 in. using silicon carbide grinding compound, grade 600.

The sintered densities of the lapped discs were determined from their weights and dimensions. Values

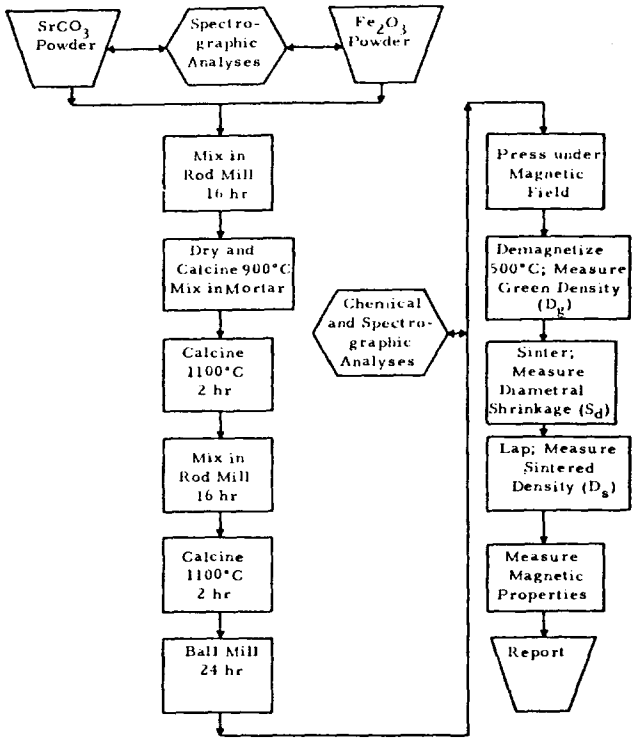

FIGURE 1. Schematic diagram of the experimental procedure.

of the thickness shrinkage (S_t) were calculated from the "green" density (D_g), the sintered density (D_s) and the diametral shrinkage (S_d), since slight warping made direct measurement of this property difficult.

The magnetic properties of the specimens were measured by the "pole-coil" method.[5] (B-H) vs H curves were plotted automatically and the intrinsic coercive force ($_iH_c$), coercive force ($_sH_c$), remanent magnetization (B_r) and maximum energy product [$(BH)_{max}$] were measured graphically. Each disc was measured in five places in order to average out local variations within the specimen.

Results and discussion

The spectrographic analyses of the raw materials and of the ferrite powders are given in Table I. The analyzed compositions of these ferrite powders were $SrO.5{\cdot}73Fe_2O_3$, $SrO.5{\cdot}77Fe_2O_3$ and $SrO.5{\cdot}76Fe_2O_3$ for Batch Nos. 1, 2 and 3, respectively, as compared with the nominal composition of $SrO.5{\cdot}5Fe_2O_3$. These differences from batch to batch are not considered to be chemically significant.

The ceramic and magnetic properties of the discs are listed in Table II; some of them are shown graphically in Figures 2 to 7. The regression equations of B_r, $_iH_c$ and $(BH)_{max}$, as functions of the mole fraction of oxygen, were computed by the step-wise method.[6] The

Table II. Ceramic and magnetic properties of $SrO \cdot 5.5Fe_2O_3$, sintered at various temperatures and in various atmospheres

Batch No.	Green density (D_g) (g/cm³)	Sintering temp. (°C)	Oxygen partial pressure (Atm)	Diametral shrinkage (S_d)(%)	Thickness shrinkage (S_t)(%)	Shrinkage ratio B/A	Sintered density (D_s) (g/cm³)	Remanent magnetization (B_r) (gauss) Mean	Remanent magnetization (B_r) (gauss) Std. Dev.	Intrinsic coercive force ($_iH_c$) (oersted) Mean	Intrinsic coercive force ($_iH_c$) (oersted) Std. Dev.	Coercive force ($_bH_c$) (oersted) Mean	Coercive force ($_bH_c$) (oersted) Std. Dev.	Maximum energy product $[(BH)_{max}]$ (10^6 gauss-oersted) Mean	Maximum energy product $[(BH)_{max}]$ (10^6 gauss-oersted) Std. Dev.
1	2.78	1160	0.0001	8.5	31.7	0.747	4.86	4098	16	1540	42	1522	40	3.69	0.04
1	2.73	1160	0.0400	9.0	28.0	0.791	4.58	3712	27	2684	30	2644	29	3.30	0.04
1	2.74	1160	0.2095	8.6	26.1	0.808	4.44	3552	30	2964	33	2924	46	2.99	0.04
1	2.74	1160	0.2095*	8.1	25.9	0.806	4.38	3510	39	2810	96	2752	72	2.93	0.06
1	2.73	1160	1.0000	7.1	22.7	0.833	4.09	3234	5	3442	23	3044	22	2.49	0.01
1	2.74	1180	0.0001	8.6	33.3	0.729	4.92	4260	31	884	9	878	4	2.71	0.03
1	2.74	1180	0.0400	9.6	31.0	0.763	4.86	4068	35	1824	17	1804	25	3.88	0.02
1	2.75	1180	0.2095	9.6	29.5	0.780	4.77	3944	39	2170	57	2140	47	3.71	0.08
1	2.72	1180	0.2095*	9.7	30.6	0.768	4.81	3954	39	1972	48	1946	48	3.70	0.07
1	2.74	1180	1.0000	9.2	28.8	0.784	4.67	3820	18	2374	55	2316	36	3.49	0.01
1	2.73	1200	1.0000	10.9	28.7	0.801	4.98	4066	17	1612	23	1592	22	3.75	0.04
2	2.75	1160	0.0001	8.0	34.0	0.718	4.92	4304	20	1352	28	1340	25	3.73	0.04
2	2.71	1160	0.0400	8.3	32.0	0.741	4.74	4066	27	2044	15	2024	15	4.00	0.07
2	2.75	1160	0.2095	7.5	26.8	0.791	4.39	3644	31	2834	50	2768	54	3.23	0.07
2	2.76	1160	0.2095*	6.7	24.0	0.815	4.17	3448	16	3026	42	2978	46	2.88	0.02
2	2.72	1160	1.0000	6.1	21.9	0.832	3.95	3188	10	3564	30	3010	22	2.41	0.03
2	2.73	1180	0.0001	8.0	35.0	0.707	4.96	4392	15	932	16	918	18	2.92	0.03
2	2.76	1180	0.0400	8.9	32.7	0.739	4.94	4304	8	1392	18	1374	13	3.83	0.00
2	2.77	1180	0.2095	8.8	31.2	0.754	4.84	4158	26	1692	18	1672	18	3.98	0.04
2	2.75	1180	0.2095*	8.3	30.3	0.760	4.69	4014	33	1940	39	1910	25	3.81	0.07
2	2.76	1180	1.0000	7.8	27.5	0.786	4.48	3756	45	2624	33	2592	44	3.42	0.08
2	2.75	1200	0.0001	8.4	33.7	0.724	4.94	4296	61	1048	26	1034	31	3.28	0.11
2	2.76	1200	0.2095	8.9	32.5	0.740	4.93	4270	39	1176	43	1164	42	3.39	0.06
2	2.71	1200	0.2095*	8.9	33.2	0.733	4.89	4186	29	1374	33	1364	33	3.72	0.09
2	2.71	1200	1.0000	8.7	31.8	0.747	4.77	4032	53	2008	54	1954	66	3.86	0.10
3	2.79	1160	0.0001	7.5	33.9	0.715	4.93	4258	39	1430	33	1412	36	3.82	0.07
3	2.76	1160	0.0400	7.6	30.5	0.752	4.65	3936	23	2564	68	2518	74	3.72	0.04
3	2.81	1160	0.2095	6.3	24.9	0.802	4.26	3508	52	3336	101	3186	69	2.97	0.08
3	2.76	1160	0.2095*	4.4	19.3	0.845	3.74	3012	39	4036	42	2876	43	2.21	0.07
3	2.78	1160	1.0000	4.0	17.8	0.856	3.67	2916	27	4300	10	2770	47	2.02	0.04
3	2.77	1180	0.0001	7.6	34.2	0.712	4.93	4400	0	1010	10	1000	7	3.17	0.04
3	2.79	1180	0.0400	8.5	32.0	0.743	4.90	4234	17	1788	13	1770	17	4.12	0.03
3	2.75	1180	0.2095	8.1	31.6	0.744	4.76	4072	20	2234	33	2200	23	3.98	0.05
3	2.80	1180	0.2095*	6.6	26.4	0.788	4.36	3630	53	2950	59	2898	68	3.17	0.10
3	2.78	1180	1.0000	6.4	26.4	0.782	4.31	3538	88	3286	147	3136	142	3.02	0.16
3	2.75	1200	0.0001	8.1	33.8	0.720	4.92	4352	18	1200	21	1190	21	3.52	0.06
3	2.75	1200	0.2095	8.7	32.7	0.737	4.90	4240	36	1660	69	1638	66	4.01	0.02
3	2.74	1200	0.2095*	7.6	31.6	0.741	4.69	3972	16	2120	93	2070	140	3.84	0.05
3	2.77	1200	1.0000	7.3	29.2	0.764	4.55	3836	62	2690	89	2602	89	3.58	0.16

*Static-air atmosphere.

following polynomial was considered as the starting model:

$$\text{Log } Y_i = a_0 + a_1 \log Ox_i + a_2 (\log Ox_i)^2 + E_i$$

where

Y_i = the observed value of one of the dependent variables B_r, $_iH_c$ or $(BH)_{max}$;

Ox_i = mole fraction of oxygen in Run i;

a_0, a_1 and a_2 are constants; and

E_i = error in Run i.

The results of these regression analyses are summarized in Table III. The results of the runs in the static-air atmosphere were not included in the regression analyses.

It is shown in Figures 2 to 7 that the presence of oxygen in the sintering atmosphere, in general, inhibits the progress of sintering. It causes a decrease in the remanent magnetization and in the sintered density, and an increase in the intrinsic coercive force. The intrinsic coercive force increases with increasing oxygen partial pressure at a different rate from both the remanent magnetization and the sintered density. As a result, at a given sintering temperature, there is an optimum partial pressure of oxygen in the sintering atmosphere that will produce a maximum $(BH)_{max}$ value. The relative magnitude of the effect of oxygen partial pressure is, of course, dependent on the sintering temperature.

Table III. Summary of the regression analysis of the magnetic properties of SrO. 5·5 Fe_2O_3 as functions of the mole fraction of oxygen in the sintering atmospheres

Property		Sintered at 1160°C						Sintered at 1180°C					
		Batch No. 1		Batch No. 2		Batch No. 3		Batch No. 1		Batch No. 2		Batch No. 3	
		Coeff.	*S.E.*	Coeff.	*S.E.*	Coeff.	*S.E.*	Coeff.	*S.E.*	Coeff.	*S.E.*	Coeff.	*S.E.*
B_r	a_0	3.512		3.503		3.467		3.582		3.578		3.553	
	a_1	−0.053	0.003	−0.098	0.002	−0.122	0.004	−0.024	0.002	−0.058	0.004	−0.076	0.006
	a_2	−0.007	0.001	−0.016	0.000	−0.020	0.001	−0.003	0.001	−0.010	0.001	−0.013	0.001
	S.Y.	0.005		0.003		0.006		0.004		0.006		0.010	
	C.V.	<1%		<1%		<1%		<1%		<1%		<1%	
	R^2	98%		99%		99%		96%		96%		94%	
H_c	a_0	3.533		3.560		3.635		3.379		3.408		3.509	
	a_1	0.074	0.006	0.204	0.009	0.182	0.007	0.066	0.006	0.250	0.012	0.226	0.010
	a_2	−0.003	0.001	0.024	0.002	0.015	0.002	−0.011	0.001	0.035	0.003	0.025	0.002
	S.Y.	0.009		0.015		0.010		0.009		0.019		0.016	
	C.V.	<1%		<1%		<1%		<1%		<1%		<1%	
	R^2	99%		99%		99%		99%		98%		99%	
$(BH)_{max}$	a_0	0.399		0.382		0.310		0.541		0.543		0.490	
	a_1	−0.114	0.004	−0.216	0.004	−0.257	0.007	−0.064	0.004	−0.069	0.010	−0.152	0.013
	a_2	−0.018	0.001	−0.042	0.001	−0.047	0.002	−0.023	0.001	−0.022	0.002	−0.037	0.003
	S.Y.	0.007		0.007		0.011		0.006		0.015		0.020	
	C.V.	1%		1%		2%		1%		3%		4%	
	R^2	99%		99%		99%		99%		92%		90%	

S.E. = Standard error in the coefficients, a_0, a_1, and a_2.
S.Y. = Standard error in *Y*.
C.V. = Coefficient of variation; i.e., the ratio of *S.Y.* to the average value of dependent variables.
R^2 = Multiple correlation coefficient.

It is shown also in Table II that there is a significant difference between discs sintered in a flowing-air atmosphere and those sintered in a static-air atmosphere. The remanent magnetization and the sintered density are generally higher and the intrinsic coercive force lower for those sintered in flowing air. The static-air atmosphere seems to behave as though it has a higher effective oxygen partial pressure than the flowing-air atmosphere.

The above-mentioned phenomena suggest that there is an oxygen transfer from the sample to the atmosphere during sintering, with the rate-controlling factor being the oxygen partial pressure in the layer immediately in contact with the surface of the sample. Thus, by increasing the flow of gas, this layer is more rapidly swept away and, consequently, the oxygen partial pressure in this layer decreases and, hence, the rate of oxygen transfer to the atmosphere increases. This

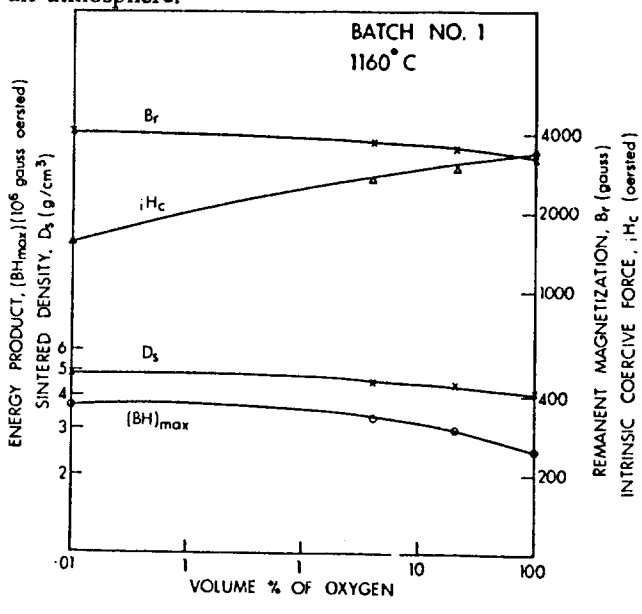

FIGURE 2. Effect of volume % of oxygen in the sintering atmosphere on the magnetic properties of SrO.5·5Fe_2O_3, Batch #1, sintered at 1160°C for 2 hrs.

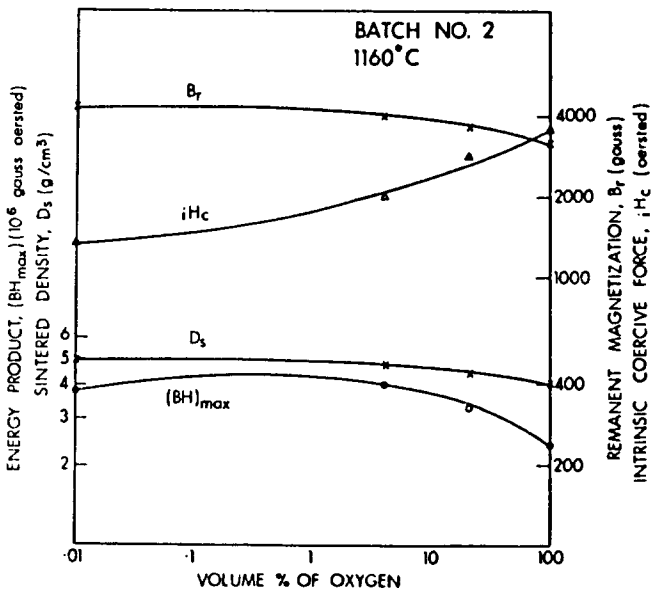

FIGURE 3. Effect of volume % of oxygen in the sintering atmosphere on the magnetic properties of SrO.5·5Fe_2O_3, Batch #2, sintered at 1160°C for 2 hrs.

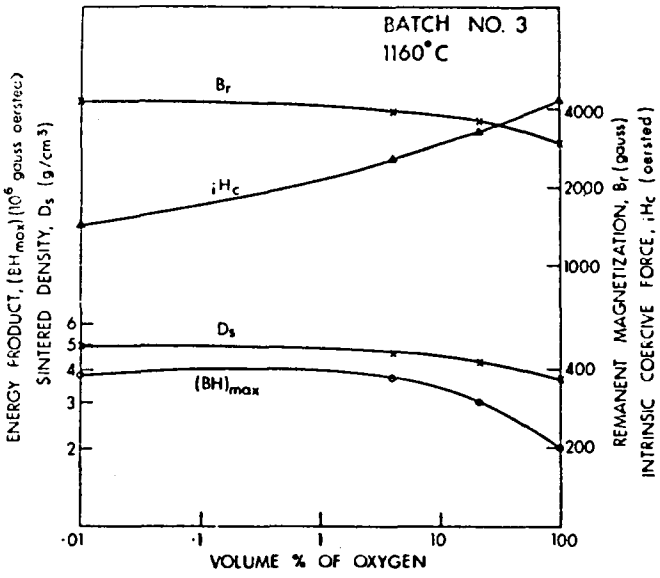

FIGURE 4. Effect of volume % of oxygen in the sintering atmosphere on the magnetic properties of $SrO.5{\cdot}5Fe_2O_3$, Batch #3, sintered at 1160°C for 2 hrs.

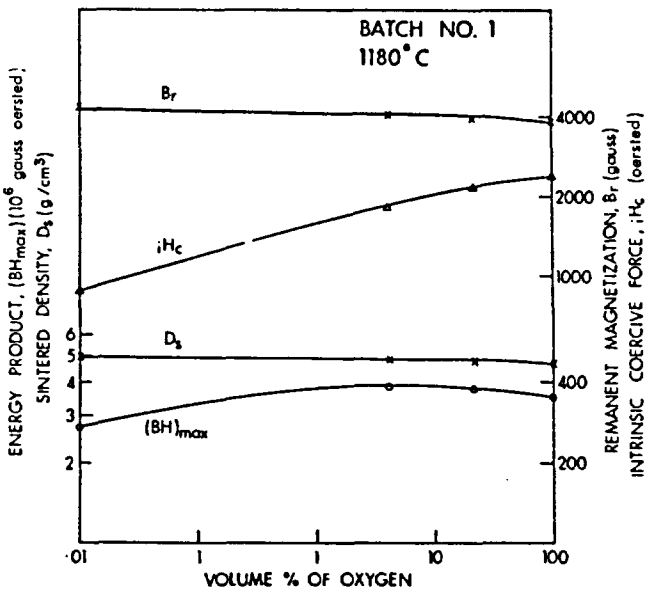

FIGURE 5. Effect of volume % of oxygen in the sintering atmosphere on the magnetic properties of $SrO.5{\cdot}5Fe_2O_3$, Batch #1, sintered at 1180°C for 2 hrs.

oxygen loss creates anion vacancies and, presumably, increases the rate of sintering. The chemical analysis of a sample from Batch No. 3, sintered at 1160°C, showed that there was no difference in the ferrous content between discs sintered in nitrogen, in nitrogen with 4% oxygen, in air (i.e., approximately 20% oxygen) and in a pure oxygen atmosphere. (These discs had been stored in air during the evaluation of their ceramic and magnetic properties.) However, when a small piece of a disc (weighing about 0.5 g) was heated to 1200°C for two hours in a nitrogen atmosphere, cooled overnight in nitrogen, and then quickly analyzed chemically, it was shown that it contained 0.16% Fe^{2+}, while another similar piece, treated exactly the same except that an oxygen atmosphere was used, was shown to contain less than 0.04% Fe^{2+}. This fact suggested

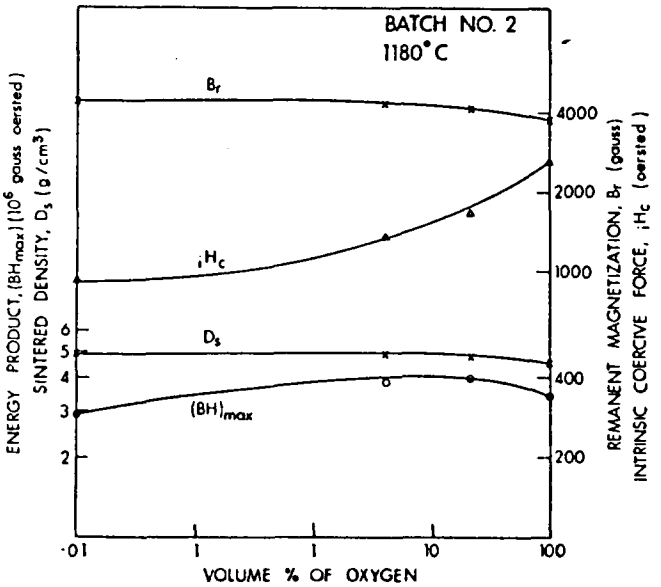

FIGURE 6. Effect of volume % of oxygen in the sintering atmosphere on the magnetic properties of $SrO.5{\cdot}5Fe_2O_3$, Batch #2, sintered at 1180°C for 2 hrs.

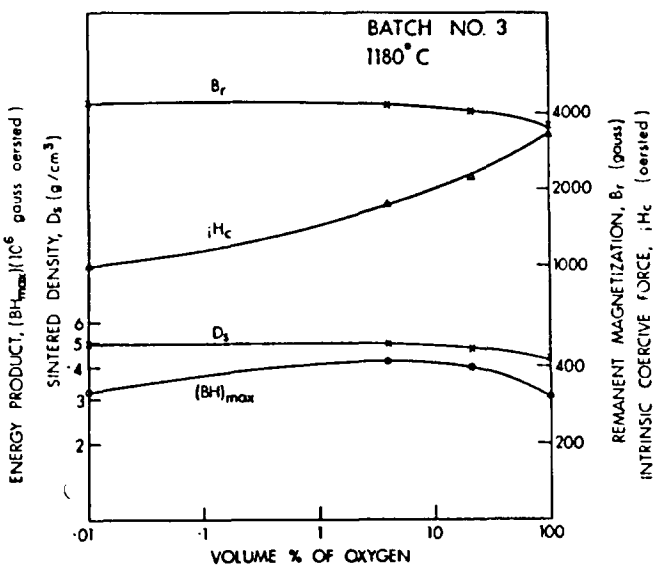

FIGURE 7. Effect of volume % of oxygen in the sintering atmosphere on the magnetic properties of $SrO.5{\cdot}5Fe_2O_3$, Batch #3, sintered at 1180°C for 2 hrs.

that some oxygen loss during sintering does occur and is enough to promote the sintering process; the sample is presumably quickly re-oxidized after exposure in the air atmosphere.

Another property that is also important is the shrinkage. The value of thickness shrinkage, S_t, (shrinkage along the crystallographic *c*-axis) ranges from 17.3% to 33.8%, while the value of diametral shrinkage along the crystallographic *c*-axis) ranges from 4.0% to 10.9%. The thickness shrinkage decreases with the increase of oxygen partial pressure. The behaviour of the diametral shrinkage with respect to the oxygen partial pressure did not exhibit a clear trend. However, the shrinkage ratio B/A, where B is defined as (100-S_t) and A as (100-S_d), increases with increasing oxygen partial pressure.

Although Batch Nos. 1, 2 and 3 show no apparent chemical differences, there are significant differences in the ceramic and magnetic properties of discs prepared from them. These discs show different levels of response to the change in oxygen partial pressure. These differences can be clearly seen in the regression coefficients listed in Table III.

Conclusions

From the foregoing discussion, it is concluded that the partial pressure of oxygen in the sintering atmosphere plays an important role in the sintering process of strontium ferrite ceramic magnets. The lower the oxygen pressure, the higher will be the rate of oxygen loss from the sample and, hence, the greater will be the increase in the rate of sintering. The intrinsic coercive force is more sensitive to variations in the oxygen partial pressure in the sintering atmosphere than are the remanent magnetization and the sintered density. Since the above effects depend approximately on the logarithm of the oxygen partial pressure, they are more noticeable at the lower oxygen partial pressures than at the higher values.

Acknowledgments

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