Effects of Additionals on the Magnetic Properties of PbO-Fe_2O_3 System

Effects of Additionals on the Magnetic Properties of PbO-Fe_2O_3 System

Hiroshi KOJIMA

The Research Institute for Scientific Measurements

(Received August 18, 1956)

Synopsis

Effects of additionals on the magnetic properties were observed in PbO–Fe_2O_3–MO system, varying the sintering conditions and the value of Fe_2O_3/PbO. Substituting PbO or Fe_2O_3 for SnO, ZnO, CdO, MgO, NiO, CuO, CoO, Cr_2O_3, B_2O_3, GeO_2, SiO_2 and ZrO_2, etc., it was found that Cr_2O_3, B_2O_3, GeO_2 and SiO_2 are effective. Best results were obtained in these systems mixed at $Fe_2O_3/PbO = 4\sim5$ by mol and sintered at 950°~1100°C. Magnetic properties of the improved PbO system oxide magnets were comparable to those of the BaO or SrO system.

I. Introduction

Oxide magnets of Magneto-plumbite type have been successfully produced industrially by Philips Research Laboratory[1] and now, Ba-ferrite is mainly used practically. Differing from Ba-ferrite, Pb-ferrite, closely related to Magneto-plumbite $Pb(Fe_{7.5}Mn_{3.5}Al_{0.5}Ti_{0.5})O_{19}$[2], has very low coercive force and in less favorable for industrial use. But PbO-system oxide magnet could be used in a unique way, if only its coercive force were to be improved to some extent, because it is easy to be manufactured due to its low reaction temperature and because the materials are also cheap, compared with BaO or SrO system.

The author attempted to improve the magnetic properties in Pb-ferrite by additionals, though the changes in magnetic properties by the addition of Bi_2O_3, TiO_2, Al_2O_3[3]-[5] had been reported already.

In this paper, the changes of magnetic properties in PbO–Fe_2O_3 system, PbO or Fe_2O_3 replaced in part with ZnO, CdO, SnO, CoO, CuO, NiO, MgO, B_2O_3, Cr_2O_3 GeO_2, SiO_2 and ZrO_2 will be reported. The results from the additionals, practically negative effects as they are, are simultaneously enumerated here in order to find a general rule for the effects of additional elements on the Pb-ferrite. But, as mentioned latter, no definite conclusion could be obtained from the experimental results in the scope of the work.

(1) J. J. Went, G. W. Rathenau, E. W. Gorter and G. W. van Oosterhout, Philp. Tech. Rev., **13** (1952), 194; Phys. Rev., **86** (1952), 424.
(2) L. G. Berry, Amer. Min., **36** (1951), 512.
(3) T. Okamura, H. Kojima and S. Watanabe, Sci. Rep. RITU, A 7 (1955), 418.
(4) H. Kojima: Sci. Rep. RITU, A 7 (1955), 502.
(5) H. Kojima: Sci. Rep. RITU, A 7 (1955), 507.

II. Experimental Procdeure

The experiments were carried out by the same procedure as mentioned in the previous papers.[3][4][5][6]

α-Fe_2O_3 prepared from $Fe(CO)_5$ and the first grade chemicals of PbO, ZnO, CdO, SnO_2, $CoCO_3$, CuO, NiO, $MgCO_3$, B_2O_3, Cr_2O_3, SiO_2 and ZrO_2, etc., were mixed in a mechanical mortar for 30 minutes at a certain mol ratio and heated in powder in the air at 900°C for 2 hours. After grinding in a mechanical mortar for 15 minutes, the powders were pressed to a cylinder form 10 mm in diameter and about 18 mm in height, under the pressure of 6 ton/cm^2. Then the specimens were sintered at 950°~1150°C for 15 minutes in air and cooled rapidly. The magnetic field was not applied during the process of pressing and heat treatment. The magnetic hysteresis loops were observed by a fluxmeter and an electro-magnet.

III. Experimental results

1. Sintering temperature

The relation of magnetic properties and sintering temperature was studied under the constant condition of the first reaction at 900°C for 2 hours. For instance, in Fig. 1 are shown the curves of magnetic properties against sintering temperature of PbO–SiO_2–Fe_2O_3 system sintered at 900°C ~1150°C for 15 minutes. The magnetic saturation $4\pi I_s$ of the specimen SiO_2 = 0% (Solid line) at the composition of (Fe_2O_3 +SiO_2)/PbO = 4.5 by mol increases with sintering temperature and the coercive force ${}_IH_c$ decreases. The remanent induction $4\pi I_r$ increases at first owing to the rise of $4\pi I_s$, but passing over the maximum point of 1050°C, it decreases again under the influence of the decrease of ${}_IH_c$. The tendency is observed commonly in all systems that $4\pi I_s$ increases and ${}_IH_c$ decreases with sintering temperature and consequently $4\pi I_r$ becomes maximum at a certain sintering temperature. But the degree of increase or decrease and the sintering temperature at which $4\pi I_r$ becomes maximum, are of course more or less different from one another, depending on the value of Fe_2O_3/PbO, the kind and amount of additionals, etc. For the specimens of SiO_2=1% in the system (Broken line), the magnetic

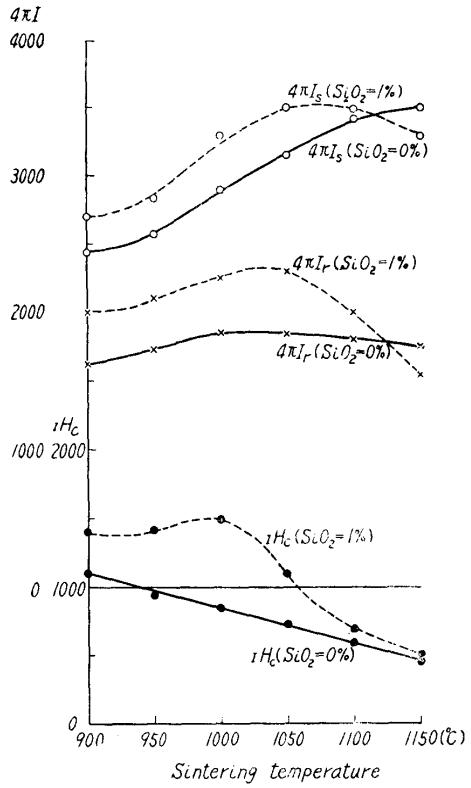

Fig. 1. Magnetic properties versus sintering temperature curves for PbO–Fe_2O_3–SiO_2 system fired at 900°C for 2 hours.

(6) T. Okamura, H. Kojima and S. Watanabe, Sci. Rep. RITU, A 7 (1955), 411.

properties are superior in general to those of SiO_2 = 0% and the maxima of $4\pi I_s$, $4\pi I_r$ and ${}_IH_c$ are found at about 1,100°, 1,050° and 1,000°C respectively.

2. Effect of Fe_2O_3/PbO

The magnetic properties of the specimens Cr_2O_3 = 0% (Solid line) and Cr_2O_3 = 3% (Broken line) fired at 900°C for 2 hours and sintered at 1,050°C for 15 minutes are illustrated in Fig. 2 for the composition of $(Fe_2O_3+Cr_2O_3)/PbO$ = 3.5~6.5. In the binary system of PbO-Fe_2O_3, $4\pi I_s$ decreases gradually from the composition of Fe_2O_3/PbO = 3.5 and the gradient of the curve becomes steeper at about 4.5 and slack again at about 5.5, while, ${}_IH_c$ increases with the ratio of Fe_2O_3 and PbO and the gradient is steep in the range Fe_2O_3/PbO=4.5~5.5, as in the case of $4\pi I_s$.

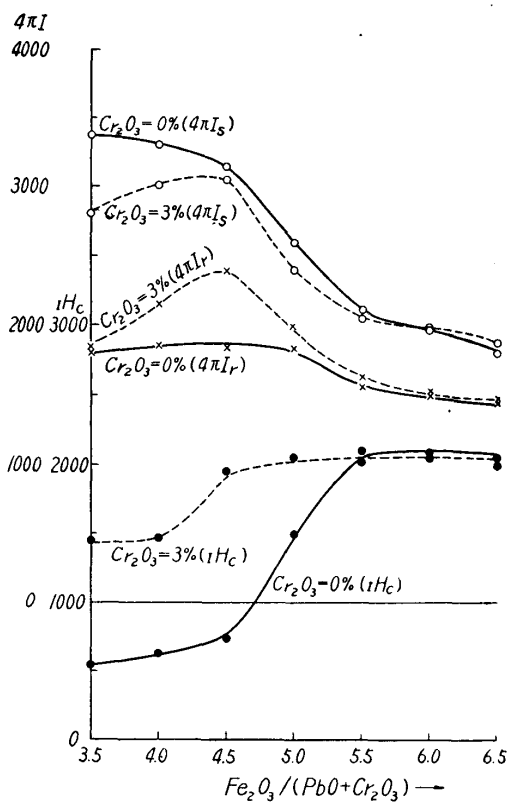

Fig. 2. Magnetic properties versus value of $(Fe_2O_3+Cr_2O_3)/PbO$ curves for PbO-Fe_2O_3-Cr_2O_3 system fired at 900°C for 2 houres and sintered at 1,050°C for 15 minutes.

Affected by both values, $4\pi I_r$ decreases gradually from the composition of Fe_2O_3/PbO=5, though a little increase is observed in the specimens of Fe_2O_3/PbO < 5.

As for the ternary system of PbO-Cr_2O_3-Fe_2O_3, ${}_IH_c$ becomes remarkably larger than that in PbO-Fe_2O_3 system in the range of $(Fe_2O_3+Cr_2O_3)/PbO < 5.5$, but the relation between ${}_IH_c$ and $(Fe_2O_3+Cr_2O_3)/PbO$ is almost the same.

$4\pi I_s$ is smaller than that of the binary system in the range of $(Fe_2O_3+Cr_2O_3)/PbO < 4.5$ but they are nearly comparable over the ratio of 4.5. Accordingly, $4\pi I_r$ becomes maximum at the point of $(Fe_2O_3+Cr_2O_3)/PbO$ = 4.5.

3. Effects of ZnO, CdO and SnO

The relationship between magnetic properties and replacing amount were studied for the PbO-Fe_2O_3 system, in which PbO was substituted partly by ZnO, CdO and SnO. Changes in magnetic properties by the sintering temperature and the value of Fe_2O_3/PbO are of course different according to the kind of additionals used. But in this paper, the magnetic properties of the specimens fired at 900°C for 2 houres and sintered at 1,050°C for 15 minutes at the composition Fe_2O_3/PbO=4.5 will be shown for an example. Properties in other cases will be guessed from these results, as mentioned above.

In Fig. 3 magnetic properties versus replaced amount of PbO by SnO, ZnO or CdO curves are given in the PbO-Fe_2O_3 system prepared under the above condition.

$4\pi I_s$ decreases in general with replaced amount, excepting a small increase in the case of SnO, and ${}_IH_c$ increases temporarily and decreases gradually again with the amount of additionals. The increasing amount is about 800 Oersted at most, so $4\pi I_r$ decreases with replaced amount, passing through a maximum point not so distinct.

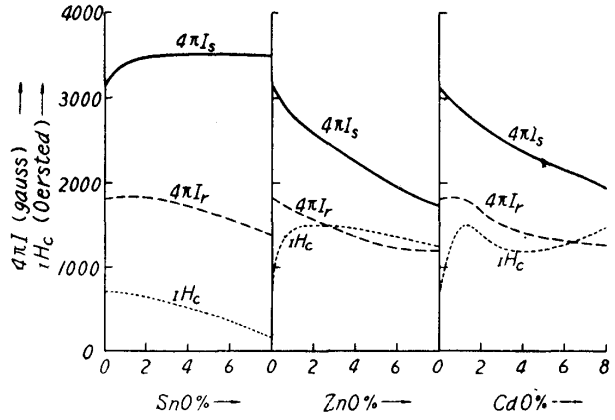

Fig. 3. Effect of additionals on the magnetic properties of PbO–Fe_2O_3 system fired at 900°C for 2 hours and sintered at 1,050°C for 15 minutes; $Fe_2O_3/(PbO + MO) = 4.5$ MO = SnO, ZnO, CdO.

4. Effect of MgO, NiO, CuO and CoO

Fig. 4 shows curves of magnetic properties versus replaced amount of PbO by MgO, NiO, CuO or CoO for the specimens prepared under the same conditions as mentioned above. $4\pi I_s$ decreases with increase of replaced amount as in the case of (3), but ${}_IH_c$ passes through a maximum point and the maximum increasing amount is about 1000 Oersted. $4\pi I_r$ also shows a maximum point at the replaced amount between 2 and 4% under the influence of ${}_IH_c$.

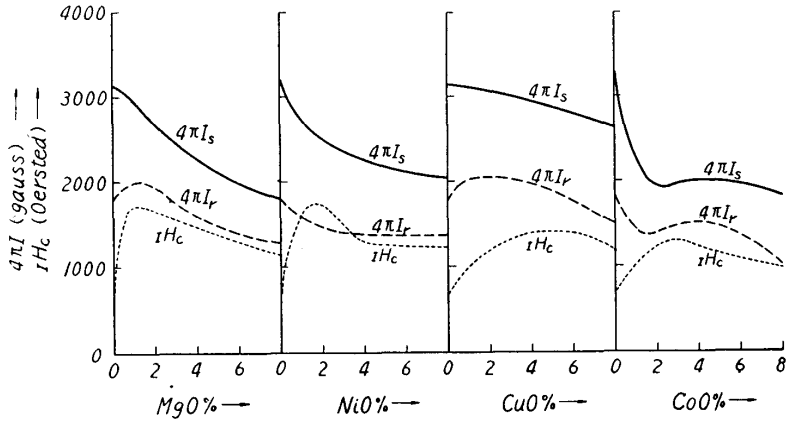

Fig. 4. Effect of additionals on the magnetic properties of PbO-Fe_2O_3 system fired at 900°C for 2 hours and sintered at 1,050°C for 15 minutes; $Fe_2O_3/(PbO + MO) = 4.5$ MO = MgO, NiO, CuO, CoO.

5. Effect of Cr_2O_3, B_2O_3, GeO_2, SiO_2 and ZrO_2

Relations between magnetic properties and replaced amount of Fe_2O_3 by Cr_2O_3, B_2O_3, GeO_2, SiO_2 or ZrO_2 are shown in Fig. 5. The conditions for preparation and

the ratio of Fe_2O_3 and PbO of the specimens are the same as in the case of (3). With the exception of ZrO_2, $4\pi I_s$ increases once and then decreases with replacing amount. ${}_IH_c$ has also a maximum point at the composition of more replaced amount than the maxmum of $4\pi I_s$.

Therefore, $4\pi I_r$ is generally improved by the certain amount of additionals.

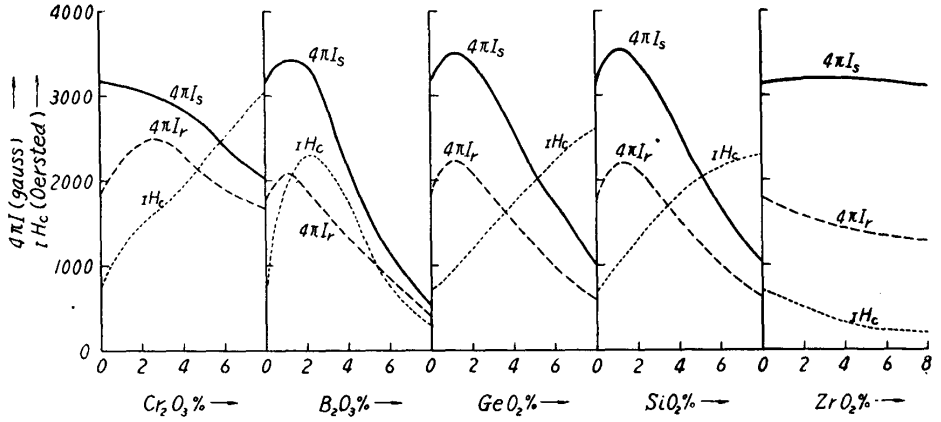

Fig. 5. Effect of additionals on the magnetic properties of PbO–Fe_2O_3 system fired at 900°C for 2 hours and sintered at 1,050°C for 15 minutes; $(Fe_2O_3+MO)/PbO = 4.5$. MO = Cr_2O_3, B_2O_3, GeO_2, SiO_2, ZrO_2.

IV. Discussion

In the present paper, the experimental results obtained only from the specimens prepared at a constant temperature and a certain vlaue of Fe_2O_3/PbO are reported, in order to avoid the complicated description.

Moreover, the selected sintering temperatures in the present work were too low to obtain the specimen having no porosity and high saturation value, with a view to preventing the decrease of ${}_IH_c$. We cannot obtain a definite conclusion on the relationship between magnetic properties and crystal structure of oxide magnet with additionals from the above experimental results. That is to say, it seems that additionals have influence not only upon their crystal structure, but also upon their reaction temperature, porosity, grain size, crystal shape and compressibility, etc.

The changes in magnetic properties by replacing amount are characteristic in each group (3)~(5), which is classified according kind of additionals used, namely, combinning to inverse spinnel (3), normal spinnel (4) with Fe_2O_3 and replacing Fe_2O_3 (5).

However, for the above reasons, the results are not due to the change in crystal structure by additionals, but they are rather obtained accidentally from the allinclusive effects, mentioned above.

It will become clearer if reference is made to our papers on the experiments in Ba- and Sr- system, or to measurements of Curie point, temperature coefficient of magnetic properties and relation between density and saturation, etc. for these ferrites, which will be published soon.

After all, it is difficult to find the common characteristic of the effective additionals and it is also difficult to presume the advantageous element from the experimental results.

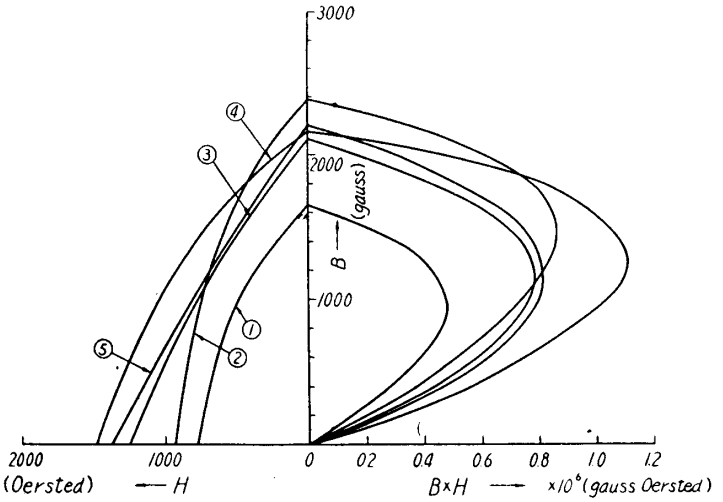

Fig. 6. Comparison of the magnetic properties for the improved PbO-magnet.

On the other hand, from the industrial viewpoint, the improved Pb-system magnets were successfully obtained in the present work and some examples of their magnetic properties are illustrated in Fig. 6. Composition and firing condition, etc. of the curves in the figure are shown in Table 1.

Table 1

No	Composition (mol)		Firing Condition	
1	Fe_2O_3/PbO = 4·5	—	900°C × 2 hrs.	950°C × 15 min.
2	(Fe_2O_3+SiO_2)/PbO = 4.5	SiO_2 = 1%	,,	1,000°C × 15 min.
3	(Fe_2O_3+GeO_2)/PbO = 4.5	GeO_2 = 2%	,,	,,
4	(Fe_2O_3+Cr_2O_3)/PbO = 4.0	Cr_2O_3 = 7%	,,	1,100°C × 15 min.
5	Fe_2O_3/BaO = 5.3	—	,,	1,150°C × 15 min.

The magnetic properties of the specimen (2), (3) and (4) containing SiO_2, GeO_2 or Cr_2O_3 respectively are comparable with the curve (5) of Ba-ferrite and surpass the curve (1) of PbO–Fe_2O_3 binary system.

summary

The relation between magnetic properties and amount of additionals for PbO-Fe_2O_3 oxide magnet was studied with an intention to make an improvement for industrial use and the following results were obtained:

(1) The best results are obtained for the specimens fired at 900°C for 2 hours and sintered at 950°~1,100°C for 15 minutes. And the best compositions are found at the mol ratio of Fe_2O_3/PbO = 4~5.

(2) $4\pi I_s$ and $4\pi I_r$ decrease and ${}_IH_c$ increases at first slightly with replacing amount of SnO, ZnO and CdO for the PbO–Fe_2O_3 system.

(3) $4\pi I_s$ decreases and ${}_IH_c$ and $4\pi I_r$ once increase with replacing amount of MgO, NiO, CuO and CoO for the PbO–Fe_2O_3 system.
(4) $4\pi I_s$, $4\pi I_r$, and ${}_IH_c$ once increase with replacing amount of Cr_2O_3, B_2O_3, GeO_2 and SiO_2 for the PbO–Fe_2O_3 system.
(5) It is difficult to find the common characteristic for the effective additionals but some effective aditionals were found practically from the experimental results, which improved the magnetic properties of PbO–Fe_2O_3 system to the values of BaO–Fe_2O_3 system.

The author wishes to thank Mr. C. Miyakawa and Mr. H. Akama for their enthusiastic help during the course of this work.