Studies on the Oxide Magnets. III : Effects of Ti0_2

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Effects of TiO_2

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Synopsis

The relationship between magnetic properties and the amount of TiO_2 was observed on TiO_2-Fe_2O_3-MO system (M=Ba, Sr and Pb) in the range $(Fe_2O_3+TiO_2)/MO=4\sim9$.

Specimens were prepared from TiO_2, oxides or carbonates of M and Fe_2O_3 obtained from $Fe(CO)_5$. Magnetic properties were weakend by the addition of TiO_2, except at the ratio of $(Fe_2O_3+TiO_2)/MO=4$, and it is considered that the apparent improvement at this composition may be due to the shift of the maximum point of magnetic properties in Fe_2O_3-MO system.

I. Introduction

Magnetic behaviours in Ba-, Sr- and Pb-ferrite by the addition of Bi_2O_3 were reported in part I[1] and part II[2]. It was concluded from these experimental results that the addition of Bi_2O_3 was effective especially on Ba-magnet. In the present paper, experimental results on the magnetic properties of these ferrites with TiO_2 will be reported.

Bi_2O_3, as mentioned in the last paper, is considered to be only an accelerating reagent for reaction or sintering and not to affect essentially the magnetic properties of the oxide magnets. On the contrary, Ti^{3+} and Ti^{4+} are both combined in spinel compounds and it is also known that the titanium oxide combines easily with iron oxide or Ba-, Sr- and Pb-oxide. Therefore, if TiO_2 were combined with these oxides, the essential effects would be expected in the magnetic properties of the oxide magnets.

That is, although the magnetic properties were weakend, it might not be due to the mixing of a free oxide of non-ferromagnetic property but to the existence of a new compound with weak ferromagnetic properties.

It is impossible to increase the magnetic properties, especially saturation, over the proper value of each magnet by an accelerating reagent for reaction. But great strides may be expected in a new ferromagnetic compound. From this point of view, the present work has been directed to the additional element, which might be combined in a new ferromagnetic phase.

II. Experimental procedure

Carbonates of Ba and Sr, Pb as PbO and Ti in the form of TiO_2 were mixed, as reported in part I and II. As for Fe, α-Ee_2O_3, obtained by the oxidation of

(1) T. Okamura, H. Kojima and S. Watanabe, Sci. Rep. RITU **A7** (1955), 411.
(2) T. Okamura, H. Kojima and S. Watanabe, Sci. Rep. RITU **A7** (1955), 418.

$Fe(CO)_5$[3], was used in order to keep a good and constant activity. Dissociation of the carbonates and reaction were performed as a powdered form at 900°~1100°C for 2 hours in the air. After cooling, they were ground and pressed into a cylindrical form 10 mm in diameter with a pressure of 6 ton/cm². Sintering was performed at 1000°~1250°C for 15 minutes in the air. The specimens were polished in both ends and the magnetic properties were observed with a flux meter, placing the specimen between pole pieces of an electro-magnet.

III. Experimental results

1. BaO-TiO_2-Fe_2O_3 system

The magnetic properties were observed on BaO-Fe_2O_3 system, in which Fe_2O_3 was replaced in part with TiO_2. If the system were represented as $BaO{\cdot}n[(Fe_2O_3)_{1-x}(TiO_2)_x]$, the observation would be carried out in the range $n=4\sim9$ and $TiO_2=0\sim10$ Mol%. First reaction and sintering were performed at 1100°C and at 1150°~1250°C respectively. In Figs. 1 and 2, $4\pi I_s$, $4\pi I_r$ and ${}_IHc$ are plotted against TiO_2% in the specimens, sintered at 1250°C for 15 minutes. Solid line represents the properties of $n=4$ and chain and dotted line show those of $n=6$ and $n=9$ respectively. Marks ○ and × are severally the values of $4\pi I_s$ and $4\pi I_r$ in Fig. 1.

$4\pi I_s$ and $4\pi I_r$ are maximum at about $TiO_2=5$% for $n=4$, and $TiO_2=1\sim2$% for $n=6$. But $4\pi I_s$ and $4\pi I_r$ for the composition of $n=9$ decrease monotonously with TiO_2%.

${}_IHc$ also decreases with TiO_2%, except a sudden rise for $n=4$ at $TiO_2=7$%, as shown in Fig. 2.

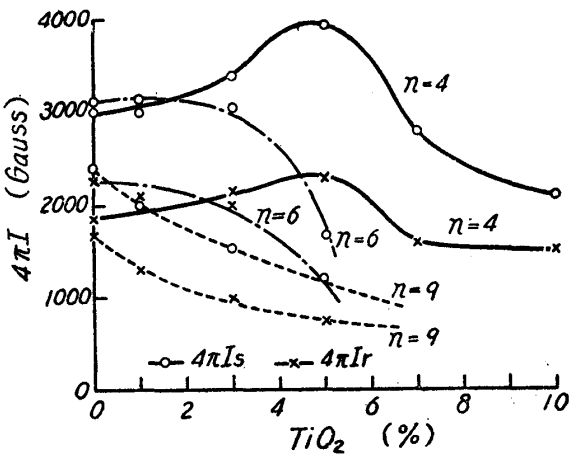

Fig. 1. $4\pi I_s$ and $4\pi I_r$ as a function of TiO_2% in $BaO{\cdot}n[(Fe_2O_3)_{1-x}(TiO_2)_x]$ sintered at 1250°C for 15 minutes at the composition of $n=4$, 6 and 9.

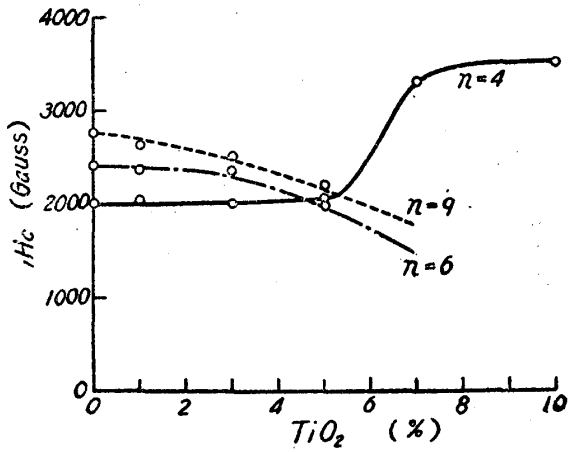

Fig. 2. ${}_IHc$ as a function of TiO_2% for each specimens in Fig. 1.

2. SrO-TiO_2-Fe_2O_3 system.

The magnetic properties of $SrO{\cdot}n[(Fe_2O_3)_{1-x}(TiO_2)_x]$ sintered at 1200°C for 15 minutes are shown in Figs. 3 and 4.

(3) T. Okamura, H. Kojima and Y. Kamata, J. App. Phys., Japan **21** (1952), 9.
H. Kojima, Res. Inst. Sci. Meas., Tohoku Univ. **2** (1952), 101.
H. Kojima, Chem. Engineer's Digest **20** (1952), 225.

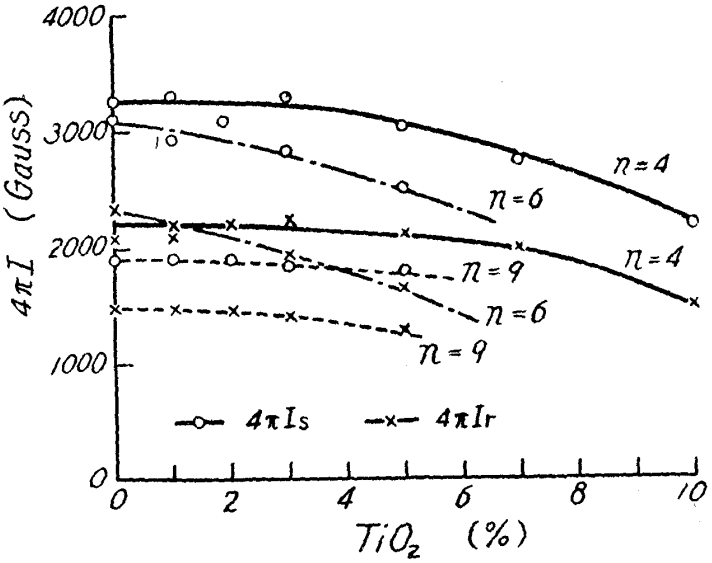

Fig. 3. $4\pi I_s$ and $4\pi I_r$ as a function of TiO_2% in $SrO{\cdot}n[(Fe_2O_3)_{1-x}(TiO_2)_x]$ sintered at 1200°C for 15 minutes at the composition of $n=4$, 6 and 9.

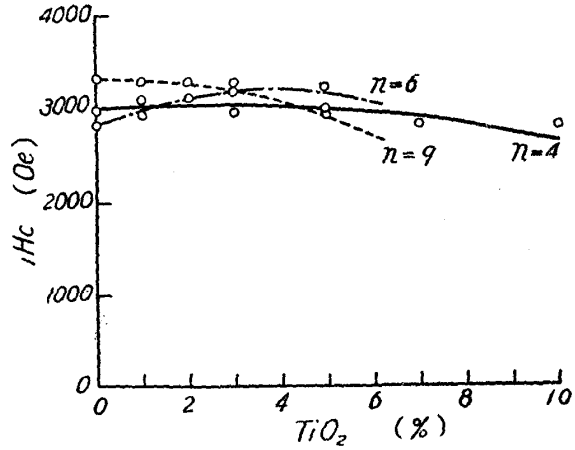

Fig. 4. $_iHc$ as a function of TiO_2% for each specimens in Fig. 3.

$4\pi I_s$, $4\pi I_r$ and the values of $n = 4$, 6 and 9 are represented in the same manner as in Figs. 1 and 2. Magnetic properties generally decrease with TiO_2 but $4\pi I_s$ and $4\pi I_r$ of $n=4$ doesn't decrease up to $TiO_2=3\%$. The descending rate of $_iHc$ is also generally gentle and value of $_iHc$ is fairly high in comparison with BaO-system.

3. PbO–TiO_2–Fe_2O_3 system

The specimens, having the composition of $PbO{\cdot}n[(Fe_2O_3)_{1-x}(TiO_2)_x]$ were heated at 900°C for 2 hours and sintered at 1100°C for 15 minutes in the air.

In Figs, 5 and 6, the magnetic properties of these specimens are plotted against TiO_2%.

The results obtained are almost similar to SrO-system; $4\pi I_s$ and $4\pi I_r$ are maximum at $TiO_2 = 3\%$ in the composition of $n = 4$ and the magnetic properties of other specimens decrease with the value of TiO_2%. $4\pi I_s$ is higher and $_iHc$ is

smaller in the present system and changes with the increase of n or TiO_2% are remakable in comparison with other systems.

III. Discussion

$4\pi I_s$ and $4\pi I_r$ become maximum at $TiO_2=5\%$ in BaO-system and at $TiO_2=3\%$ in SrO- and PbO-system at the composition of $n=4$ by the addition of TiO_2. And the magnetic properties of $n=6$ and 9 decrease monotonously with the amount of TiO_2.

In BaO–TiO_2–Fe_2O_3 system, the magnetic properties near the composition of BaO 20%, TiO_2 5%, Fe_2O_3 75% seem to be slightly improved as compared with BaO–Fe_2O_3 system. However, if the maximum points of the curves are doubled, the values of magnetic properties of $MO\cdot n[(Fe_2O_3)_{1-x}(TiO_2)_x]$ in the present paper almost coincide with those of $MO\cdot nFe_2O_3$, reported in part I[1] and II[2], neglecting the value of n. For instance, the maximum value at $n=5.5$ in $4\pi I$-n diagram of BaO–Fe_2O_3 system is almost equal to the value at $TiO_2=5\%$ in Fig. 1.

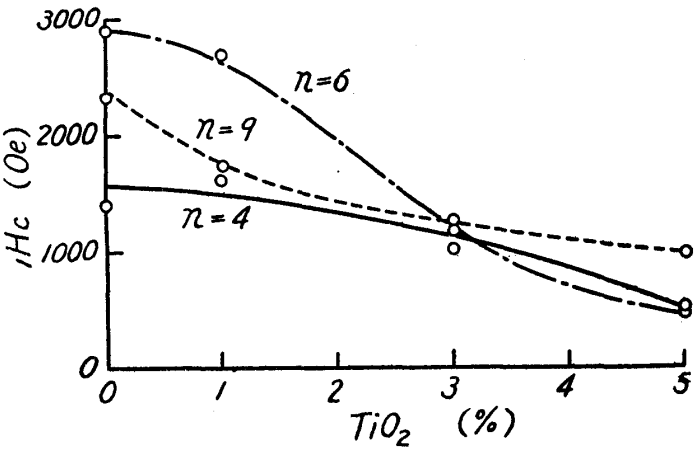

Fig. 5. $4\pi I_s$ and $4\pi I_r$ as a function of TiO_2% in $PbO\cdot n[(Fe_2O_3)_{1-x}(TiO_2)_x]$ sintered at 1100°C for 15 minutes at the composition of $n=4$, 6 and 9.

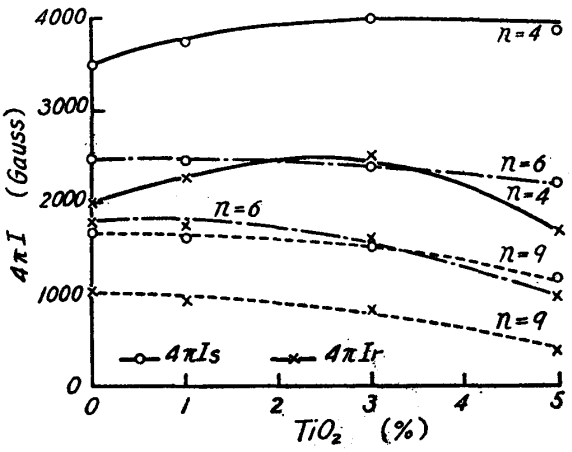

Fig. 6. $_iHc$ as a function of TiO_2% for each specimens in Fig. 5.

Now, if TiO_2 combines only with MO and the amount of $MTiO_3$ were so small that the effect on the magnetic properties could be neglected, the properties of the system should be decided by the compound of $MO\cdot n'Fe_2O_3$. Here, n' is simply calculated to $n(1-x)/(1-n)$, and TiO_2 content may be represented by $nx/(n+1)$ from the above assumption. Then, n' is calculated numerically from the above formulas as a function of TiO_2% in the case $n=4$, 6 and 9, which is illustrated in Fig. 7.

The maximum points of $4\pi I_s$ and $4\pi I_r$ on the specimens of $n=4$ are obtained at the composition of $TiO_2=5\%$ in BaO–TiO_2–Fe_2O_3 system and $TiO_2=1\sim3\%$ in SrO–TiO_2–Fe_2O_3 and PbO–TiO_2–Fe_2O_3 systems, as shown in Figs. 1, 3 and 5. In these cases, the values of n' are found from Fig. 7 to be $n'=5$ in $TiO_2=5\%$ and $n'=4\sim4.5$ in $TiO_2=1\sim3\%$ respectively, and the obtained values of n' coincides with each maximum point in BaO–Fe_2O_3, SrO–Fe_2O_3 and PbO–Fe_2O_3 systems reported in part I and II, For $n=6$ and 9, it can be seen that the magnetic properties does

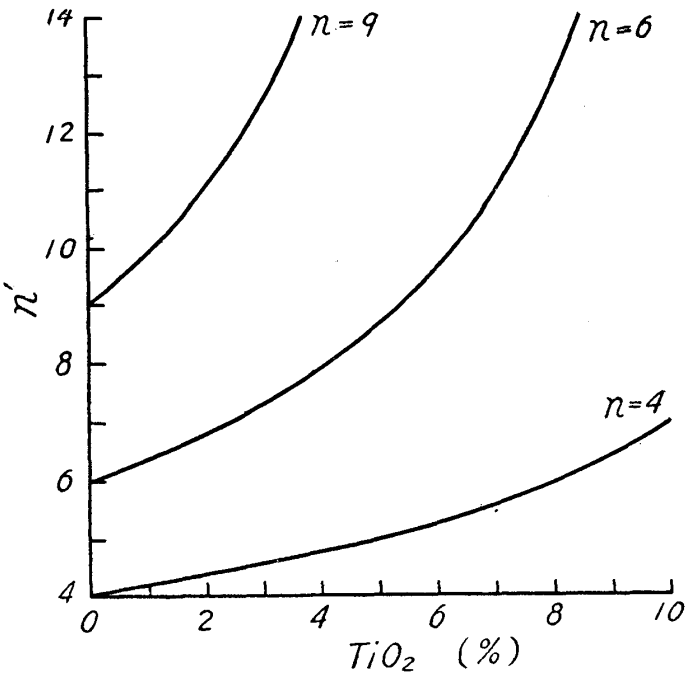

Fig. 7. Relations between n and n' as a function of TiO_2%.

not increase by the addition of TiO_2, because the curves of $n=6$ and 9 do not cross the line $n'=5$ or 4~4.5 in Fig. 7.

It may be impossible to determine from the present experiments what form of compound can be found in $MO-TiO_2-Fe_2O_3$ system but it seems clear from the above discussion that the increase in magnetic properties by the addition of TiO_2 is only due to the shift of the maximum points in $MO-Fe_2O_3$ system, owing to the consumption of MO combined with TiO_2.

Summary

The magnetic properties of $MO\cdot n[(Fe_2O_3)_{1-x}(TiO_2)_x]$ were observed in M=Ba, Sr and Pb in the range $n=4\sim9$ and $TiO_2=0\sim10\%$ and the following results were obtained:

(1) The magnetic properties were weakend by the addition of TiO_2, except in the case of $n=4$.

(2) In Ba-ferrite, $4\pi I_s$ and $4\pi I_r$ became maximum at $TiO_2=5\%$ and ${}_IHc$ at $TiO_2=7\%$ at the composition of $n=4$.

(3) In Sr- and Pb-ferrite, $4\pi I_s$ and $4\pi I_r$ were maximum at $TiO_2=1\sim3\%$ at the composition of $n=4$.

(4) Magnetic properties were apparently improved by the addition of TiO_2 in the composition of $n=4$, but it is considered that the maximum points of magnetic properties in $MO-Fe_2O_3$ system only shift by the consumption of MO, owing to the addition of TiO_2.

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