

On the Method of Sample-Sealing in Thermo- Magnetic Analysis

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Abstract

In this paper are reported, (1) when carrying out the thermo-magnetic analysis of an open sample of titanomagnetite, it undergoes oxidation or reduction according to the pressures of the rarefied air and the temperatures to which the sample is exposed and therefore, the values of the magnetization and the Curie point thus obtained are not identical with those of the original sample, and (2) when the sample is sealed in a quartz tube evacuated to as low as 10^{-4} mmHg, no chemical change takes place in the sample. Also reported are the relations between the Curie point, the lattice constant, and the intensity of magnetization at the room temperature which have been obtained by this method of sample-sealing with titanomagnetites from different localities in Japan.

Introduction

The Curie points of a ferromagnetic material have been determined by most investigators by heating a sample of the material in a rarefied air or in a nitrogen gas. However, by virtue of oxygen molecules in the air or those mixed as an impurity within the nitrogen gas, the sample may undergo oxidation during the heating and therefore the sample during the heating may no longer be that material which is identical with the sample before the heating. Consequently the Curie point thus determined may be the Curie point of the material different from the original. In order to find out how the magnetic and the related characteristics of ferromagnetic minerals in a given rock change with temperature, we need a condition in which no chemical change takes place in the materials of the sample during the measurement.

The measuring apparatus used in the present investigation is a sensitive thermo-magnetic balance equipped with a quartz spring and working by a non-uniform magnetic field of an electro-magnet. The electro-magnet was excited only when measurement of magnetization was carried out, because a continuous excitation gives rise to experimental difficulties. The samples used are titanomagnetites $(\text{Fe}_{2-2x}^{+++} \text{Ti}_x^{++++} \text{Fe}_{1+x}^{++}) \text{O}_4$, where $0 < x < 1$, from igneous and sedimentary rocks

from different localities in Japan.

In the first place, the result of thermo-magnetic analysis will be reported on open samples affected by oxidation and reduction, and in the second place, on sealed samples free from these chemical changes.

1. Experiments on open samples

Experiment 1.1. One milligram of a powder sample (about 2 microns in size) of the titanomagnetite from the Genbudo basalt* was taken in an open quartz basket hung from the lower end of the quartz spring of thermo-magnetic balance and was heated in the air at a pressure of 10^{-1} mmHg. At the intermediate temperatures from the room temperature up to 310°C , the intensity of magnetization J_s was determined in the field of 3000 Oe. After the value of J_s at 310°C was measured as practically zero, the sample was kept for 30 minutes at this temperature, and then left to cool down to the room temperature, J_s at the intermediate temperature being also measured. The J_s vs. T relation, where T is the temperature, obtained in this first process is shown by the curve $abcdec'b'a'$ (Fig. 1). Just after the measurement of J_s at point a' was taken, the heating and determination of J_s were again carried out until the temperature reached 395°C , at which J_s assumed a very small value. Similarly the sample was kept for 30 minutes at this temperature and then left to cool down to the room temperature. The result obtained in this second process is shown by the curve $a'b'c'efgc''b''a''$. The third and fourth processes are shown in the figure. At all temperatures with the exception of 310, 395, 450 and 515°C where the sample was kept for 30 minutes, no time elapsed except the short interval of time needed for the measurement of intensity of magnetizations.

The following fact may be worth noticing: (1) When the sample was kept for 30 minutes at 310° , 395° and 450°C , J_s increased from zero or almost zero value to 6.0, 7.7 and 12.5 C.G.S./gr respectively. But when the sample was kept for the same period of time at 515°C , J_s did not increase with time. (2) Along the paths, $ec'b'a'$, $gc''b''a''$ and $ijc'''b'''a'''$, the change of J_s with respect to T was reversible. (3) The later the process, the greater the value of J_s at a given temperature, the value of J_s at the room temperature found in the last process being over two times the initial value.

For the purpose of finding the effect of time upon the increase of J_s , an experiment was made with another powder sample of titanomagnetite from the same Genbudo basalt by fixing the temperature at 350°C . We adopted two kinds of pressure, 10^{-2} and 10^{-3} mmHg, at which the sample was exposed. The period of the experiment was about 64 minutes. The result is shown in Fig. 2, in which we can see that when the pressure was 10^{-2} mmHg J_s increased proportionally to

* From Genbudo, a place of interest being famous for the beautiful columnar joints of basalt, situated near the coast of the Sea of Japan, Hyogo Prefecture, West Japan.

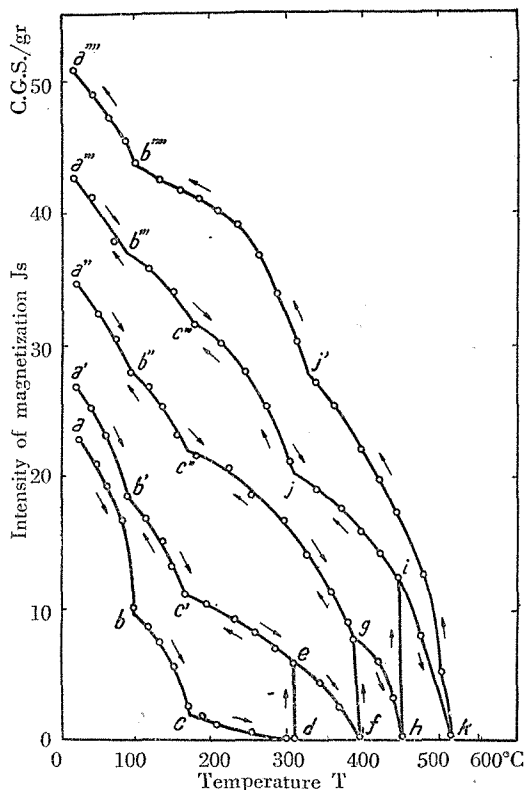


Fig. 1. Thermo-magnetic analysis of a titanomagnetite sample from the Genbudo basalt which is exposed to a rarefied air of a pressure of 10^{-1} mmHg.

artificial magnetite the Curie point and the saturation magnetization increase with the ratio of $\text{Fe}^{+++}/\text{Fe}^{++}$ of the magnetite. Consequently it is very likely by for our experiment 1.1 that the oxygen molecules in the rarefied air of a pressure of 10^{-1} mmHg oxidized the sample when it was kept for 30 minutes at 310° , 395° and 450°C and the oxidation increased J_s at a given temperature (Fig. 1.). Whereas in experiment 1.2. the rarefied air of a pressure as low as 10^{-4} mmHg deprived the sample at 1000°C of its combined oxygen and this heat treatment had the effect of reducing the ratio of $\text{Fe}^{+++}/\text{Fe}^{++}$ of the sample in a manner opposite to that in which the oxidation increased it.

Here it is to be noticed that the maintenance of the pressures of 10^{-1} , 10^{-2} , 10^{-3} and 10^{-4} mmHg were made possible by a steady pumping throughout the experiment. It may be worth noticing that in our experiments a rarefied air having a pressure of 10^{-1} mmHg was nearly equivalent in the oxidizing effect to

the square root of time and that when the pressure was 10^{-3} mmHg J_s increased with the square root of time, asymptotically approaching a stationary value.

Experiment 1.2. Having adopted a still reduced pressure of 10^{-4} mmHg, we heated the sample 350°C at which it was kept for hours. But no increase in J_s was found. The sample was then heated up to 1000°C at which the sample was kept for hours and subsequently cooled down to the room temperature, J_s being measured at the intermediate temperatures. It was found then that the Curie points and J_s in the cooling process were much lower than those obtained in the preceding heating, and further that the greater the period of time during which the sample was kept at 1000°C , the greater the decrease of the Curie point and J_s . The lowest Curie point ever reached by this procedure was found to be -40°C .

Pouillard¹⁾ and Akimoto²⁾ have confirmed that in the case of an

the commercial nitrogen gas at a pressure of one atmosphere which was purchased in Kyoto City in about 1950.

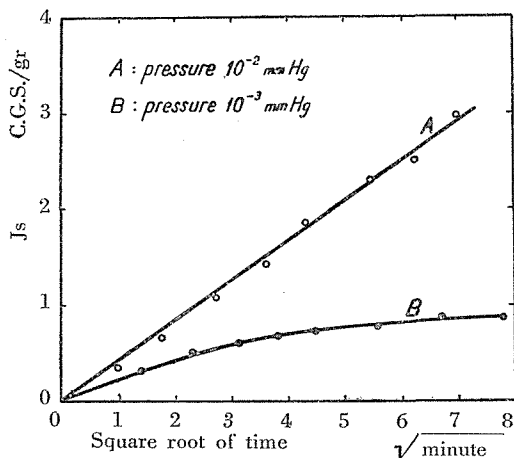


Fig. 2. Increase of magnetization J_s with time for the powder samples (titanomagnet from the Genbudo basalt) of 2μ in size exposed to a constant temperature of 350°C in a rarefied air.

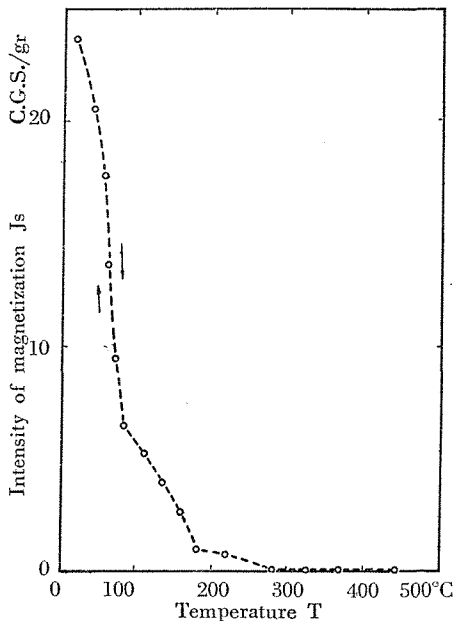


Fig. 3. Experiment on a sealed sample of titanomagnetite from the Genbudo basalt.

2. Experiments on sealed samples

In the preceding paragraph it has been pointed out that if we carry out the thermo-magnetic analysis for the open sample in a rarefied air, it undergoes oxidation or reduction according to pressure during the thermal treatment, which means that the sample thus thermally treated is no longer identical with the original sample. Therefore, we have to carry out the experiments in the condition in which no chemical change mentioned above takes place. In order to prevent oxidation and reduction or to allow them to occur in the smallest degree, we finally came to seal the sample into an evacuated quartz tube of a small diameter with its dead space as small as possible. The residual air in the dead space was evacuated prior to heating to as low as 10^{-4} mmHg.

The sample thus sealed was heated from the room temperature up to 1000°C and at the intermediate temperatures J_s was measured. After having kept the sample at this high temperature for 5 hours, the sample was then cooled to the room temperature, J_s being also measured. It was then confirmed that the J_s vs. T curve obtained in this thermal treatment was quite reversible as shown in Fig. 3. This fact proves that the sealing of sample in the manner mentioned above has produced no appreciable chemical change in the mate-

rial of the sample. This method of sample-sealing is to be recommended in the thermo-magnetic analysis, when oxidation and reduction must be avoided.

By adopting the sealed sample, the authors have carried out experiments to clarify how the Curie point is related with the lattice constant and J_s at the room temperature. The samples of titanomagnetite are those taken from the igneous and sedimentary rocks from many localities in Japan, and besides these natural samples, artificial samples were also made use of. From all the samples of which the thermo-magnetic analysis and the determination of Curie points have been made, those which have proved to be single-phased have been selected. Then these selected samples have been subjected to the NORELCO X-ray analysis and the lattice constants have been calculated. The values of intensity of magnetization at the room temperature, denoted by J_s' , Curie point θ and lattice constant a thus obtained are given in Table I. The θ vs. a and the θ vs. J_s' relations are graphically shown in Figs. 4 and 5. In Fig. 4, it can be seen that the Curie point decreases linearly as the lattice constant increases. From the least squares adjustment, the θ vs. a relation has been found as follows.

$$\theta = 2857 - 5833 (a - 9.000)^\circ\text{C} \dots\dots\dots (1),$$

$$\pm 64 \quad \pm 146$$

where a is expressed in \AA and the annexed errors are the mean errors. In Fig. 5

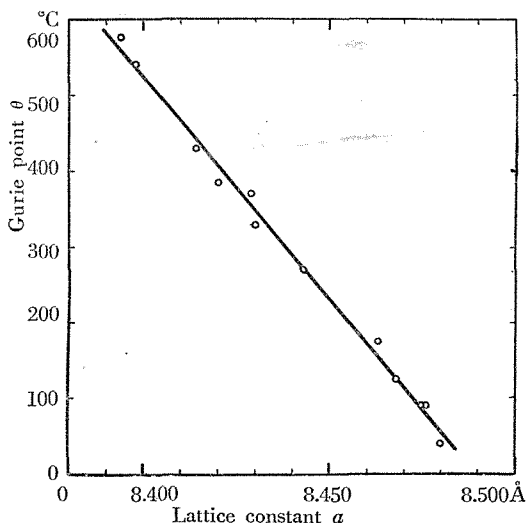


Fig. 4. Curie point vs. lattice constant relation obtained for single-phased titanomagnetites the Curie points having been determined by sealing the samples.

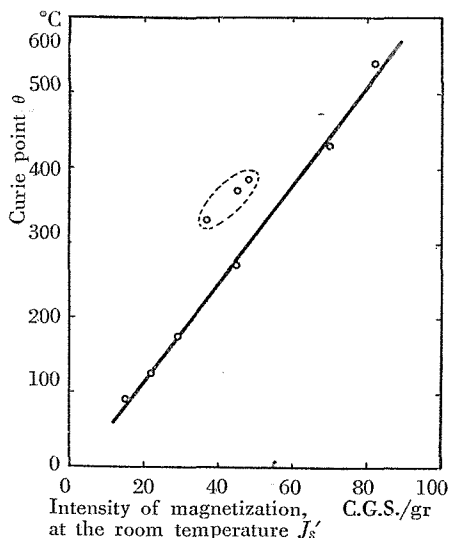


Fig. 5. Curie point vs. intensity of magnetization at the room temperature relation obtained for the same single-phased titanomagnetite, the values of J_s and θ having been determined by sealing the samples.

it is noticed that, with the exception of the three plots enclosed by a dotted ellipse, θ also increases linearly as J_s increases. The shift of these three plots from the line representing this linearity is in the direction of decreasing J_s and this is very likely due to attachment of some amount of silicates (non-magnetic) to the sample used. Calculated from the amount of the shift, the mass of these non-magnetic parts is on the average 32.7% of that of the magnetic part. Even the seven samples, whose plots of θ vs. J_s' lie beautifully on and along the straight line in the figure, may be suspected of accompanying some amount of silicate materials. But, if so, the attachment of these silicate materials should be so systematic as to agree with the linear relation. However, this is quite inconceivable, and therefore it is very likely that these seven samples may be nearly free from such non-magnetic matters. The least squares adjustment for this linear relation has been done, by omitting the three plots mentioned above, with the following result:

$$\theta = -19.7 + 6.67 J_s' \text{ } ^\circ\text{C} \dots \dots \dots (2),$$

$$\pm 11.1 \pm 0.22$$

where J_s' is expressed in C. G. S./gr. The straight line in Fig. 5 has been drawn according to (2).

Table I. Measurements on titanomagnetites from igneous and sedimentary rocks from different localities in Japan a =lattice constant, θ =Curie point J_s' =intensity of magnetization at the room temperature

No.	Locality	Rock or Samples	$a(\text{\AA})$	$\theta(^\circ\text{C})$	$J_s'(\text{C.G.S./gr})$
1.	Muroto-misaki	Gabbro	8.394	575	—***
2.	Mikasa-yama	Andesite	8.398	540	81
3.	Ojima	Andesite	8.476	70	15
4.	Ibaraki	Azuki tuff	8.420	330	37
5.	Bôsô Peninsula	Tuffaceous sandstone, No. 23	8.430	385	48
6.	"	" No. 01	8.429	370	45
7.	Genbudô	Genbudô basalt, No. 1*	8.480	40	—***
8.	"	" No. 2*	8.475	90	—***
9.	"	" No. 3*	8.468	125	22
10.	"	" No. 4*	8.463	175	29
11.	—	Artificial No. 1**	8.443	270	45
12.	—	" No. 2**	8.414	430	70

N.B.—It is to be noticed here that the andesite from Mikasa-yama is normally and the four rocks from Ojima, Ibaraki, Bôsô Peninsula and Genbudô are all reversely magnetized, the gabbro from Muroto-misaki being not yet determined as to its direction of magnetization.

Reference

- 1) E. Pouillard, *Ann. de Chem.*, **5**, 164, 1950.
- 2) S. Akimoto, *Jour. Geomag. Geoele.*, **6**, 1, 1954.

* Nos. 1, 2, 3 and 4 are the ferromagnetic minerals magnetically separated from a powder sample of the Genbudô basalt at 50°, 100°, 150° and 200°C respectively.

** These are the artificial titanomagnetites manufactured in our laboratory.

*** Experiments for the measurement of J_s' were not carried out owing to the silicates clearly observed under a microscope as attaching to the powder specimens of dimensions of 1 to 10 microns. It was almost impossible to detach these silicates.