107. Exsolution of Titanomagnetite and Its Time Effect on Rock-Magnetism. III

Effects of Enduring Temperature and Slow Cooling

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Several years ago, Vincent and Phillips, and Kume, Sasajima, and I commenced independently the investigations concerning stability relation of an Fe₃O₄-TiO₂Fe₂O₄ solid solution. And almost at the same time, both published their results showing them in phase diagrams. The diagrams, however, differed slightly from each other. The former authors found the existence of an eutectoid point in an intermediate solution, whereas we interpreted the solvus as a smooth curve.

Since then we have carefully reexamined the investigation but our previous solvus was found to require no appreciable correction to be added, and we have reached the conclusion that the most likely solvus curve in the solid solution may be the same as given in Fig. 1. Consequently, my discussion described in the following is established on the basis of this solvus curve.

In the figure, an auxiliary line OP which separates the phase diagram into A and B regions is drawn in such a manner that it may bisect the angle between the temperature axis OY and the Curie point axis OX. As shown in the diagram, this line and the solvus curve meet at two points t₁ and t₂ whose ordinates are called here the critical temperatures T₁ and T₂ respectively. If a line y=T (where T is an arbitrary temperature) which is parallel to x-axis is drawn on the diagram, it will intersect the solvus curve twice at the points a and b, and the line OP at t. From the definition of the phase diagram, Curie points of the two titanomagnetites which exsolve at T are represented by the abscissae of the points a and b. Since the auxiliary line has such a nature that at any point on this line the abscissa and the ordinate...
are equal to each other, the temperature of the phase splitting can be regarded as the abscissa of the point \( t \) (or \( x_t \)).

In the first place, we confine our discussion to the simplest case when the phase splitting is allowed to occur only once at a given temperature \( T \), and any further occurrence during the subsequent cooling is prevented. The manner in which these exsolved titanomagnetites acquire magnetism depends greatly upon the temperature \( T \) at which the phase breaks up, and the cooling starts.

(1) When the exsolution occurs at a temperature higher than the critical temperature \( T_i \), both of the exsolved phases may have thermo-remanent magnetism during the cooling, because the relation \( x_a < x_b < x_t \) is satisfied, and the cooling of such magnetites can be regarded as the so-called field cooling through their Curie points.

(2) In case the phase splitting takes place in the range between the critical temperatures \( T_1 \) and \( T_2 \), it is evident from the figure that one of the exsolved phases has Curie point lower and the other higher than the temperature of the exsolution, i.e., \( x_a < x_t < x_b \). Consequently, in the cooling only the former phase can have thermo-remanent magnetism, while the latter has not.

(3) When the phase splitting is to take place at temperature lower than \( T_2 \), the exsolved phases have their Curie points all higher than the temperature from which the cooling starts, as revealed by the relation \( x_t < x_a < x_b \). Hence neither of these two phases can occur.

The Néel's establishments on the magnetic fluctuation after-effect, show that such magnetites as have been formed at temperature lower than their Curie points, have their relaxation time of magnetization exceedingly prolonged. Accordingly, the magnetization of these phases belonging to (2) or (3) may be said to be quenched, being left in a substantially demagnetized state, so long as an especially strong field is not applied upon it.

When the facts described at the above-mentioned three cases are brought together in the same diagram, they can easily be summarized in the following manner; when the composition of an exsolved phase is represented by a point on the full line part of the solvus curve, the titanomagnetite may be said to be occupied by the thermo-remanent magnetism, whereas, in case the composition considered is represented by a point on the broken line part of the solvus curve, we can see that the titanomagnetite is vacant in thermo-remanent magnetism.

We are next to consider the influence of time upon the magnetization of rock at various temperatures. This effect has not been taken into account in the previous ideal cases. Let us start supposing that the temperature of rocks, after the phase splitting of magnetites, remains at \( T \) for some interval of time.
(1') When $T$ is found at temperature above $T_1$, the endurance of temperature of whatever duration, will not give rise to any essential change in the mechanism of magnetization, because exsolved phases $a$ and $b$ will acquire the magnetization in the subsequent cooling in the manner just described in the previous case.

(2') Next, consider a case when the rock is kept at a temperature $T$ between $T_1$ and $T_2$ during some interval of time. Although we have two titanomagnetites in equilibrium with this temperature, one of them whose Curie point is lower than $T$ has mechanism of magnetization quite identical with that already stated in (1), (2), or (1'), and therefore, no description is needed.

But the magnetization of the other titanomagnetite whose Curie point is higher than $T$, though for the simplicity's sake, concluded to be left unmagnetized in case (2), can not be summarized in the same way. Because those magnetic domains whose relaxation time is shorter, or comparable to the duration, enter into the magnetic equilibrium state, acquiring their magnetization in the direction of the effective field. The number of magnetic domain in such a state increases according to increasing interval. This kind of magnetization was first discovered by Thellier and was called by him the isothermal remanent magnetism.

(3') In case $T$ is found at a region below $T_2$, two magnetites are to be born at a temperature lower than their Curie points, therefore, only a similar process to that stated above case (2') enables the titanomagnetite to acquire magnetization.

Néel has also pointed out in one of his papers that pace with which such magnetization at a given temperature proceeds with time, depends greatly upon the temperature difference from its Curie point in such a manner that the pace becomes slower as the temperature difference increases, the relaxation time being shown by a rapidly increasing function of the latter. This temperature difference corresponds to the length of line $bt$ or $at$ on our diagram.

As is recognized from the diagram, $bt$ increases in length as the point $b$ recedes from the point $t_1$, descending along the solvus curve, and in a similar manner $at$ also increases in length as the point $a$ does from the point $t_2$. When this fact is taken into consideration, it is reasonable to assume that a titanomagnetite whose composition is found on the curve in the vicinity of the point $t_1$ or $t_2$, has a shorter relaxation time compared to the one farther away from $t_1$ or $t_2$, or in other words, the effect of time on the magnetization is greater in the former, and smaller in the latter.

Now let us bring together all these influences of time which occur
at every temperature on the diagram. We can see that the region of the solvus curve occupied by magnetization expands while that unoccupied contracts in the manner shown in Fig. 2. The arrows show the direction along which the full line part of solvus curve expands with time.

Among the influences of various enduring temperatures upon rock-magnetism, the influence of that in the vicinity at room temperature is of great importance, because the time interval during which the rock has been submitted to the influence in the field, is considered to be of the order of age of the rock. In an ancient rock the duration is prolonged so long that we can not discuss the magnetization without inquiring the role it plays in the process. However, such magnetism could be accounted for on a mechanism quite similar to the case (3') if the effect of prolonged duration is taken into account. As is evident from the relation $at < \beta t$ in Fig. 1, the temperature differences between the Curie point and the enduring temperature are especially smaller in one of the phases with lower Curie point than in the other phase, with the rate of magnetization exceedingly greater in the former phase. In our previous papers we reported the rocks whose magnetization depends upon the phases with the lowest or next lowest Curie point and upon none of the others. The most appropriate example demonstrating this behaviour is shown by Figs. 6-8 in our second paper. The results can well be explained on the basis of Néel's theory in the following way; phase with higher Curie point has so extremely prolonged relaxation time of magnetization that even the interval from tertiary epoch to the present is not yet sufficient, consequently almost the whole phase being left in an unmagnetized state. Whereas the relaxation time of the phase with lower Curie point is shorter or nearly as long as the time interval, hence some of the phases have magnetized.

The following descriptions in a summarized form are given in the order which may probably represent the sequence of the rock-magnetism in its evolution.

(A) In all effusive rocks which we have dealt with so far, titano-magnetites with intermediate Ti-contents are the magnetic minerals at the time of formation, their magnetization being what is called...
the thermo-remanent magnetism.

(B) On cooling there takes place a phase splitting by which the original magnetite breaks up into Ti-rich and Ti-poor magnetites, the original thermo-remanent magnetism vanishing at the same time. However, so long as the composition of the exsolved phase is found on the full line part of the solvus curve, magnetization to be acquired by these phases may still be regarded as thermo-remanent magnetism which, however, is demagnetized more or less in its geological period or is renewed by further exsolution. On the other hand, if their composition is found on the broken line part of the solvus curve, this magnetization may be taken as a case of the isothermal remanent magnetism which increases with the increase of duration.

(C) On further cooling and after the cooling, exsolution phases newly born on the broken line part of the solvus curve (or unmagnetized) acquire the isothermal remanent magnetism in such a manner that the phase with lowest Curie point is magnetized first and then the phase with the next lowest Curie point and so on, all in order under increasing Curie point.

(D) Phase splitting into a pair of titanomagnetites, one with the Curie point at about 50°C and the other 540°C is the energy lowest state of the exsolution at ordinary temperature, and a titanomagnetite with any other Curie point is nothing but a transitional or metastable one at that temperature. And so long as the rock would be kept under a condition not very different from what has been in the field, the splitting of such a magnetite will continue to occur towards the above-mentioned final phases, which, however, can no longer be allowed to be occupied by the thermo-remanent magnetism.

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References