1972, *Phys. Earth Planet. Interiors* **5**, 87–89. North-Holland Publishing Company, Amsterdam

ACTIVATION ENERGY OF UNMIXING OF TITANOMAGHEMITE

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Received 2 June 1971

Both titanomagnetite and titanomaghemite show a characteristic irreversible increase of J_s and Curie temperature on heating in air. The former is due to multiphase oxidation of titanomagnetite, and the latter to unmixing of titanomaghemite to magnetite and Ti rich phases. Applying a phenomenological theory of rate process (STREET and WOOLLEY, 1949) to thermomagnetic data, it is found that the unmixing of titanomaghemite is described by a rate process with a single activation energy. The activation energy E_s thus obtained is 0.033 eV, which is about one order of magnitude smaller than that obtained for multiphase oxidation of titanomagnetite by CREER *et al.* (1970).

1. Introduction

Recently, a characteristic irreversible thermomagnetic curve have attracted interest among rock magnetism researchers (WASILEWSKI, 1969; OZIMA and LARSON, 1970; OZIMA and OZIMA, 1971; CREER *et al.*, 1970; SANVER and O'REILLY, 1970; SCHAEFFER and SCHWARZ, 1970). The irreversible thermomagnetic curve is found in most of submarine basalts and also in some of subareal basalts. The thermomagnetic curve is characterized by the irreversible increase of J_s and Curie temperature on heating. From the comparison of thermomagnetic curves for vacuum and air heating, OZIMA and OZIMA (1971) concluded that the irreversible change in submarine basalts is generally due to unmixing of Ti rich titanomaghemite to Fe rich magnetic phases (magnetite) and Ti rich phases such as ilmenohematite and pseudobrookite, whereas multiphase oxidation of titanomagnetite is a more likely cause for the irreversible thermomagnetic curve in subareal basalts. The former change is observed both on air and vacuum heating, but the latter is only seen on air heating. They also suggested that suboceanic environment is more preferable for production of titanomaghemite.

CREER *et al.* (1970) have estimated the activation energy for the irreversible change in the case of some basalts from Azores Islands. The samples studied by them do not show the irreversible change when the experiment is carried out in vacuum. The latter fact clearly indicates that the irreversible change observed by Creer *et al.* is due to multiphase oxidation of titanomagnetite. Hence, the activation energy estimated by them must refer to oxidation processes of titanomagnetite.

In a recent paper, SANVER and O'REILLY (1970) have called attention to the difficulty of distinguishing between titanomagnetite and titanomaghemite by conventional methods such as chemical analyses or ore microscopic observation. In addition, the similar appearance of the thermomagnetic curves in air for titanomagnetite and titanomaghemite seems to be responsible for the confusion in some papers in distinguishing between the two phases. Hence, it would be desirable to examine further the two irreversible processes. In the present paper, the activation energy is estimated for unmixing of titanomaghemite. It is hoped that the comparison of this activation energy with that obtained by CREER *et al.* (1970) would be useful to elucidate the difference of the two processes.

2. Theory

We apply phenomenological equations of rate process to interprete the irreversible process, as was done by CREER *et al.* (1970). STREET and WOOLLEY (1949) have shown that if a rate process is characterized by a single activation energy E, the time variation of the process then can be expressed as an exponential function of time, that is,

$$A-B\,e^{-\lambda t}. \tag{1}$$

If there is a continuous spectrum of activation energy, the process will vary as a logarithmic function of time, such as

$$A'+B'\log t. \tag{2}$$

In submarine basalts, the irreversible change is due to unmixing of titanomaghemite to magnetite and Ti rich phases such as ilmenohematite or pseudobrookite. Since magnetization of Ti rich phases are much weaker than that of magnetite, the process may be regarded that each elementary process of unmixing contributes a certain amount of magnetite and nonmagnetic phases resulting in the net change in the magnetization due to the difference between the original titanomaghemite and the newly produced magnetite. This simplification enables us to make a direct comparison between the observed thermomagnetic data and the above phenomenological theory. The change of magnetization in the unmixing process would be expressed either by an exponential function of time (eq. (1)) or by a logarithmic function (eq. (2)), depending on the spectrum form of the activation energy.

3. Analyses of experimental data

The time variation of the magnetization was measured at $H = 3000$ Oe in vacuum of about 10^{-3} torr at two different temperatures, that is, at 350 °C and at 455 °C for drilled Mohole basalt EM-7. From thermomagnetic analyses both in air and vacuum, chemical analyses, X-ray analyses and microscopic observation, it is confirmed that the ferromagnetic constituent in EM-7 is exclusively titanomaghemite (Ozima and Larson, 1970). Experimental data on magnetization were then plotted in two different diagrams, one as an exponential function of time (eq. (1)) and the other as a logarithmic function (eq. (2)) (figs. 1a, b). By comparison of these figures, it is seen that the experimental data are better represented by eq. (1), or the data lie almost on a straight line in fig. 1b. This may be reasonable, because the unmixing process is essentially an ionic diffusion process among certain lattice sites; the process can be better represented by a single or at least a few activation energies rather than by a continuous spectrum.

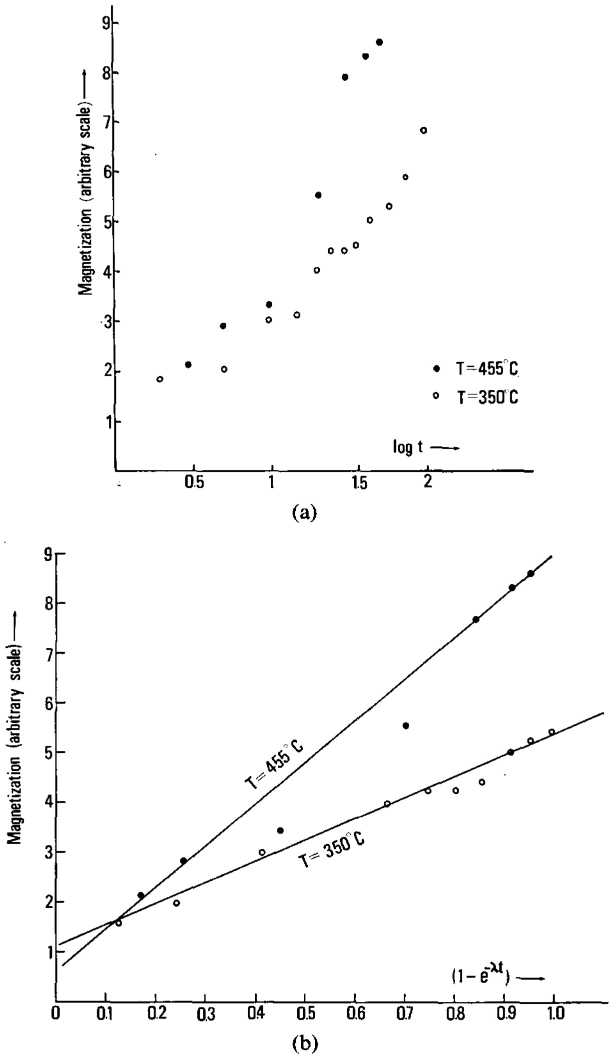

Fig. 1. Magnetization, measured at $T = 350$ °C and 455 °C in vacuum (10^{-3} torr), as a function of (a) log t and (b) $(1-e^{-\lambda t})$.

Assuming that the unmixing process can be expressed by eq. (1), the change in the magnetization M can be expressed as (Street and Woolley, 1949)

$$M = M_0+\alpha(1-e^{-\lambda t}). \tag{3}$$

In this equation, λ denotes the time constant of the rate process and is given by

$$\lambda = C\,e^{-E_s/kT}, \tag{4}$$

in which E_s, C, k and T denote the activation energy, a numerical constant, Boltzman's constant and the temperature, respectively. It is easy to see from eqs. (3) and (4) that several measurements of magnetization at each of two or more different temperatures can determine λ and E_s uniquely. Using the data shown in fig. 1, we obtained the following values for λ and E_s:

$\lambda = 0.055\ \mathrm{min}^{-1}$ for $T = 350\ ^\circ\mathrm{C}$,
$\lambda = 0.060\ \mathrm{min}^{-1}$ for $T = 455\ ^\circ\mathrm{C}$,
$E_s = 0.033$ eV.

4. Discussion

The activation energy obtained above is more than one order of magnitude smaller than that obtained by CREER *et al.* (1970), the latter value being 0.5 eV. The sample studied by Creer *et al.* has almost the same Ti/Fe ratio as that of the submarine basalt studied here. Hence, the titanomaghemite in the submarine basalt is approximately similar to the one which will be obtained by "maghemitization" of the former. The surprisingly low activation energy is in accordance with the unstable character of titanomaghemite.

Since the irreversible increase of J_s and Curie temperature is clearly a function of the competition between the specimen temperature and the degree of unmixing of titanomaghemite or multiphase oxidation of titanomagnetite, the latter process may sometimes be more conspicuous even at the same temperature, depending on heating rate and other experimental conditions. However, the comparison of the activation energy between the two processes clearly shows that, in general, unmixing of titanomaghemite is more important at lower temperatures than multiphase oxidation of the corresponding (having the same Ti/Fe as the titanomaghemite) titanomagnetite, in accordance with the common observation that the former process usually takes place below 300 °C, whereas the latter process seldom occurs around this temperature. It is then reasonable to expect that, in naturally occurring rocks, unmixing of titanomaghemite (if any) proceeds more easily than oxidation of titanomagnetite. This may explain the common occurrence of titanomagnetite in rocks, whereas the occurrence of titanomaghemite is rather limited to submarine basalts and some subareal basalts. In the latter cases, the presence of water appears to be essential to stabilize titanomaghemite (OZIMA and LARSON, 1970).

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