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Transition of SiO_2 in Diatomaceous Earth to Cristobalite

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§1. Introduction

It is known that silicon dioxide in diatomaceous earth transforms to cristobalite at high temperature.(1) One of the present authors (T. N.) studied on the diatomaceous earth from Suzu-shi in the Noto Peninsula, by means of the measurement of electric conductivity.(2) In the present report, some theoretical considerations on the electric conductivity data are made, together with another confirmation of this transition by an observation of thermal expansion.

§2. Relation between electric conductivity and porosity

On the relation between the electric conductivity of porous materials and their porosity, many experimental investigations have been reported.(3) But the results are more or less diverse and the theoretical treatment is difficult.

R. Landauer(4) presented an equation giving the electric conductivity of binary metallic mixture σ_m as a function of the conductivities of the components σ_1, σ_2, and their volume fractions x_1, x_2 :

$$\sigma_m=\frac{1}{4}\left[(3x_1-1)\sigma_1+(3x_2-1)\sigma_2+\sqrt{\{(3x_1-1)\sigma_1+(3x_2-1)\sigma_2\}^2+8\sigma_1\sigma_2}\right]. \qquad (1)$$

To apply this equation to porous materials, the variables are transfered as follows :

$\sigma_m\rightarrow\sigma_a$(apparent conductivity of porous material),

$\sigma_1\rightarrow\sigma_t$(true conductivity of the material),

$\sigma_2\rightarrow 0$(conductivity of air),

$x_2(=1-x_1)\rightarrow P$(porosity).

Then a very simple equation is obtained :

$$\sigma_a=\left(1-\frac{3}{2}P\right)\sigma_t. \qquad (2)$$

This equation between σ_a and P is a straight line cutting P-axis at $P=2/3$ and σ_a-axis at $\sigma_a=\sigma_t$.

Figure 1 shows the electric conductivity of the diatomaceous earth fired at 900~1200°C for three hours as a function of its porosity, details of measurement being described in reference (2). The solid curve in figure 1 runs along the dotted straight line drawn from a point $P=2/3=66.7\%$ in the region of $P=50\sim60\%$, which shows that the variation of conductivity with porosity in this range is merely due to the sintering of the sample. For $P<50\%$, the experimental curve departs far from the theoretical one, suggesting that the

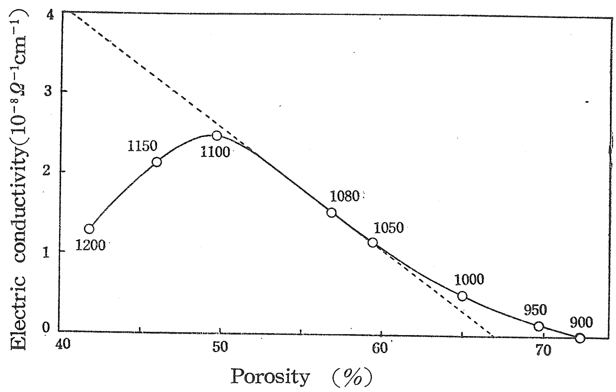

Fig. 1. Electric conductivity at 250°C of fired diatomaceous earth versus its porosity. Firing temperatures are written on the circles in °C. Dotted line shows equation (2).

change of structure of the material other than sintering is arising. This consideration insures the conclusion of the previous paper.

For $P>60\%$ also, the experimental curve deviates from the theoretical one. This is interpreted as follows. The equation (1) is based on the assumption that each material particle or crystallet is spherical and can be considered as if surrounded by a homogeneous medium of the mixture. The fact that the conductivity in equation (2) vanishes at $P=2/3$ means that in the porous material, in general, the material particles or crystallets, assumed to be spherical, are scattered separately in the isolated states for the porosity higher than this value, and can no longer have the

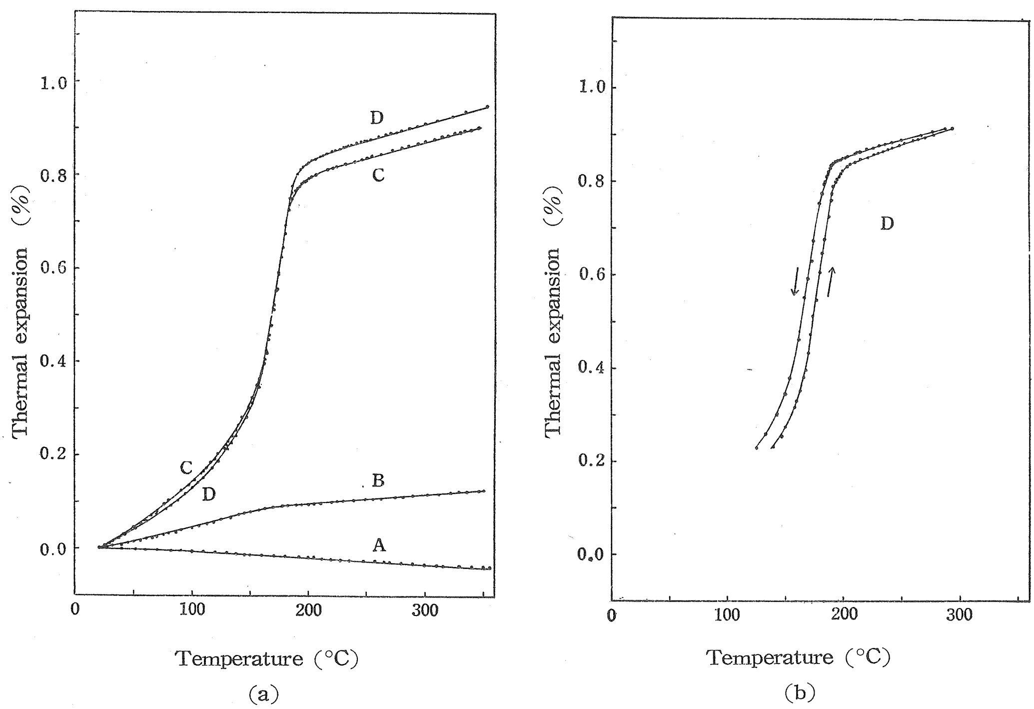

Fig. 2. Thermal expansion of fired diatomaceous earth relative to standard rod.

Curve	Firing temperature	Standard rod
A	600°C	Quartz
B	1000 〃	Diatomaceous earth fired at 600°C
C	1100 〃	〃 〃
D	1200 〃	〃 〃

continuous structure for conducting electricity. In the case of the diatomaceous earth, however, it has so fine reticular structure that it still can be thought continuous even beyond this point, and the conductivity becomes larger than that expected from equation (2). In a word, equation (2) does not hold in such a region of high porosity.

§3. Observation of thermal expansion

It is well known that cristobalite can exist as α-cristobalite at room temperature and, when heated, transforms to β-cristobalite at 180~270°C. Therefore, if the diatomaceous earth fired at high temperature contains much cristobalite, its coefficient of thermal expansion must change at that temperature. This was observed by C. Kawashima.[5] The present authors investigated this phenomenon by means of the Honda-Satô's differential dilatometer.

The sample rods of 5.0 or 8.0 cm long and 4.8~5.0 mm in diameter were sawed out from a natural rock. They were fired at 600, 1000, 1100, and 1200°C for three hours in an electric furnace, then cooled to room temperature, and mounted in the dilatometer. As the standard rod, a quartz rod was used for the sample fired at 600°C, and 600°C-fired sample rod, for the samples fired at 1000~1200°C. The heating rate was about 1°C/min in the vicinity of the transition point.

The results are shown in figures 2 and 3. In figure 2, ordinates denote the expansion of samples relative to standard rod devided by their initial length. The gradient of the curve gives the coefficient of differential expansion. In figure 3, the coefficients thus obtained from figure 2 (a) are shown for the samples fired at 1000°C and 1200°C.

For the sample fired at 600°C, the thermal expansion is almost linear, or the coefficient is nearly constant, suggesting no transformation to be arising. The sample fired at 1000°C shows a change of expansion at about 170°C. It is attributed to the $\alpha \rightarrow \beta$ transformation of cristobalite slightly contained in the sample. In Kawashima's result the expansion of the sample fired at 1000°C is almost linear. For the samples fired at 1100°C and 1200°C, the change of expansion is distinct, evidently indicating that these samples are abundant in cristobalite. This result is similar to Kawashima's one, but the change is larger for the present samples. The transformation takes place during 140~190°C for the sample fired at

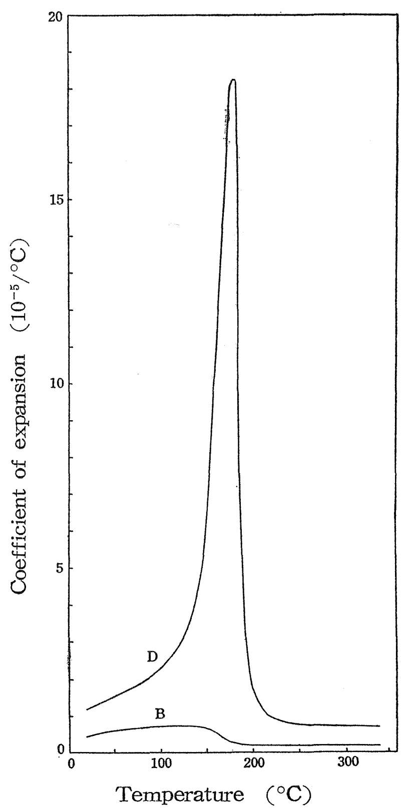

Fig. 3. Coefficient of differential expansion of fired diatomaceous earth estimated from figure 2. Labels on the curves have the same meaning as in figure 2.

1100°C, and during 140∼195°C for the one fired at 1200°C. Thus the transition point of cristobalite in diatomaceous earth is somewhat lower than that of pure crystal. It may be an effect due to impurities contained in the diatomaceous earth. The heating curve and cooling curve show a hysteresis in figure 2(b).

§ 4. Summary

(1) The relation between the electric conductivity and the porosity of the diatomaceous earth fired at temperatures below 1100°C satisfies an equation derived from Landauer's one. The samples fired over 1100°C does not satisfy the above relation. This is attributed to the transition of this material to cristobalite.

(2) The thermal expansion of the fired samples was observed by means of the Honda-Satô's differential dilatometer. For the samples fired over 1100°C, the coefficient of expansion changes at 140∼190°C corresponding to the $\alpha \rightarrow \beta$ transformation of cristobalite.

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