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Electric Conductivity of Diatomaceous Earth

By

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§ 1. Introduction

Diatomaceous earth is used for various purposes, such as heat insulation, an addition to concrete, a filter-aid, an absorbent and a carrier for catalyser. Its physical and chemical properties were minutely investigated by C. Kawashima and Y. Shiraki from a ceramic viewpoint.(1),(2)

In the Noto Peninsula, Ishikawa-ken, there are thick diatomite deposits, which can be sawed out as a large natural rock and are used as sawed and calcined bricks or cooking-furnaces. They also make bricks or cooking-furnaces pressed and calcined from powdered earth. M. Ono and S. Kondo,(3) Kawashima and Shiraki,(1) and Kawashima(2),(4) reported their researches on the diatomaceous earth in this district. The present author has studied this material concernig the electric conductivity and obtained a result consistent with that which the previous investigators had found from the other physical properties.

§ 2. Method of experiment

Samples were made of the natural rocks from the deposits in Iizuka, Shôin-machi, Suzu-shi in the Noto Peninsula. The dimension of samples thus prepared was about 3 cm × 2 cm wide and 1 cm thick. A sample fired at an appropriate temperature was cut into two pieces, which were coated with graphite on both faces, put between metal plates, and mounted in a nichrome wire electric furnace as shown in Fig. 1. Then their electric conductivity was measured in air. The temperature in the furnace was measured by means of an alumel-chromel thermocouple and a millivoltmeter, and was kept constant by a thermoelectric temperature regulator. As the electric furnaces for firing, a nichrome wire furnace was used under 1000°C, and a sillicon carbide one over 1000°C.

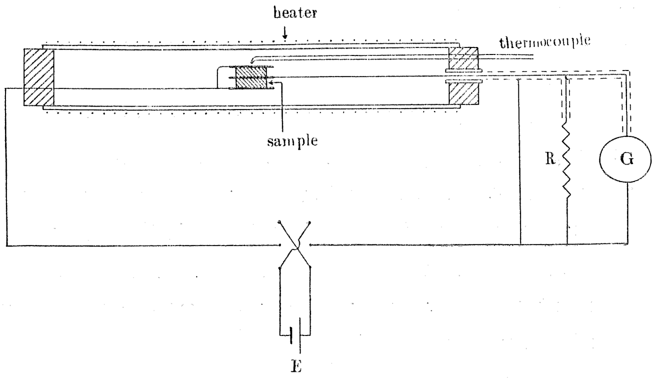


Fig. 1.—Schematic diagram of the apparatus.

The circuit for measurement, at the beginning, consisted of a battery E, galvanometer G, a shunt resistance R, and the sample (Fig. 1), and afterward the battery was replaced with a D. C. voltage stabilizer. In the late stage of the investigation a standard resistance, D. C. amplifier and a microammeter were used (Fig. 2). The electric resistance of the sample being very high, the wire joining the sample and the galvanometer (Fig. 1) should be an air-wire. In this case, however, this wire needed to be supported by a stand at the outlet from the furnace, lest it should touch the lid of the furnace. So this part of the wire was doubly insulated from ground partitioning by metal plate which was connected to the leading wire between the battery and the galvanometer.

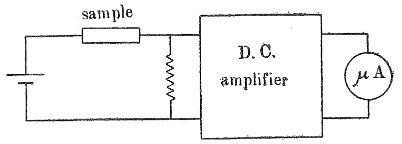


Fig. 2.—Circuit for measurement.

§ 3. Preliminary experiment

It was intended at first to measure the conductivity of an unfired sample at room temperature, but it was too unstable to give a definite value of conductivity. For example, a sample showed its conductivity of $1.8\times10^{-6}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ one day and $1.2\times10^{-6}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ the next day, while it rised to $3.0\times10^{-6}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ when the vicinity of the sample was breathed upon. On the other hand the intensities of current in one direction and the reversed were not the same. These phenomena are ascribed to the following factor. The diatomaceous earth being a porous material, it adsorbs on its internal surface of pore considerable quantity of water, which varies with the humidity of the air and it shows no constant value of conductivity. Moreover the diatomaceous earth in this district, as Kawashima and Shiraki indicated(1a), contains much alkali and alkali earth compounds, which may compose an electric cell with water and electrodes and give rise to the apparent anisotropy of conductivity.

A fired sample has less ability of adsorption(1c) but still adsorbs a little amount of water, so the conductivity was thereafter measured at 200∼450°C. The upper limit of the temperature was determined so as the electrodes not to oxidize in the air. Even at high temperatures some dependency of current on directions was observed, that obliged to take the average of currents in both directions, from which the conductivity was computed.

To get rid of the influence of surface current in the measurement of high resistance, it is a usually employed method to wind a guard wire round the side of sample and allow the electricity which leads over the surface of the sample to pass back to the electric source without going through the galvanometer. In the present investigation also this guard wire was tested and found to have desired effect at room temperature, but at the dried state over 200°C it made no difference whether the guard was put or not. Rationally considered, a porous material, as in this case, has so wide internal surface besides external that it may be meaningless to give consideration only to the external surface current. So the measurements were carried out without the guard wire.

Applying a voltage to the sample, a large current flows at first, but it decreases rapidly and approaches to a stationary value. Fig. 3 is an example measured at room temperature on a fired sample. The relation between current and time after voltage of 1.5 V was applied is the curve-1. Then reversing the polarity of voltage the curve-2 was obtained. Reversing the polarity again and again, the curves -3 and -4 were obtained.

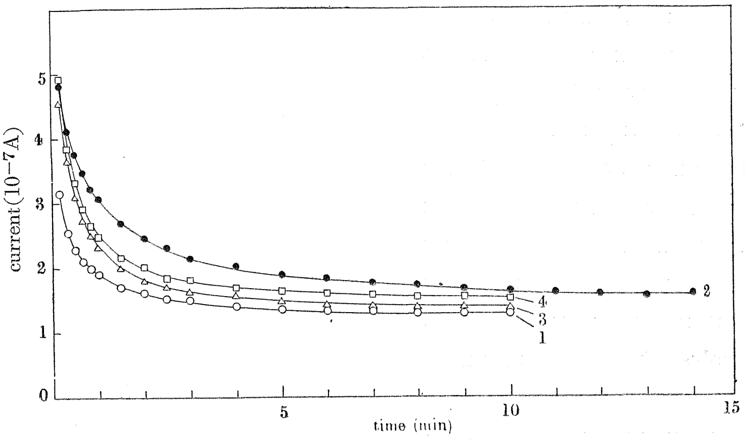


Fig. 3.—Transition current at room temperature.

Thus this transition current is influenced sensitively by the hysteresis of the sample, but the values of the stationary current are almost equal. Only they are different with its polarity, that was mentioned above. Let i_∞ be the stationary current and i the current at time t. These curves are approximately expressed by

$$i-i_\infty=At^{-n}, \qquad (1)$$

where A and n are constants depending upon temperature. The values of n for these curves are as follows:

curve-1 : 0.8, -2 : 0.7, -3 : 1.0, -4 : 1.0.

The expression (1) is similar as that for the polarization current, and the values of n are consistent with the observed values for it, suggesting that one part of the current is due to the polarization of ions or similar phenomena. Though this transition phenomenon falls off at high temperature, the conductivity was computed from the almost stationary values of the current seven minutes later after switching in.

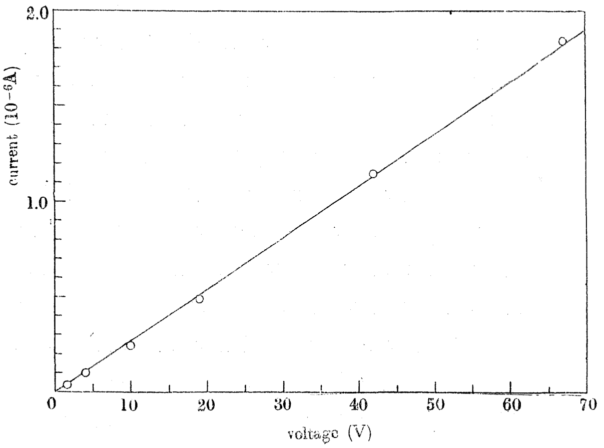


Fig. 4.—Current-voltage characteristic at 325°C for a sample fired at 1000°C.

Next the voltage-dependency of conductivity was examined. The current-voltage characteristic measured at 325°C on the sample fired at 1000°C is given in Fig. 4, which shows approximately the ohmic law, the small deviation from which may perhaps be caused by inconstancy of temperature.

§ 4. Results and discussions

In order to examine the influence of firing time, the temperature dependencies of conductivity of samples fired at 500°C for 1~10 hours were measured. Fig. 5 is a conductivity-temperature curve for a sample fired for four hours. These of different hours of firing have nearly equal slope and tendency except more or less difference in absolute value, therefore only one example are represented for fear of the complexity of diagram. The curve in Fig. 5 is nearly a straight line, and between the conductivity σ and the absolute temperature T the relation:

$$\sigma = Be^{-\frac{\varepsilon}{kT}} \qquad (2)$$

holds, where B is a constant, k the Boltzman's constant and ε the activation energy. The value of ε computed from the slope of the line is about 0.9 eV. To express the influence of firing time, conductivities at 350°C of samples fired for various hours are shown in Fig. 6. These values were not measured at 350°C but gained by interpolation from the conductivity-temperature curves such as in Fig. 5. And these points are the mean of the measured values on two samples. This shows that the samples fired for more than three hours has little variety.

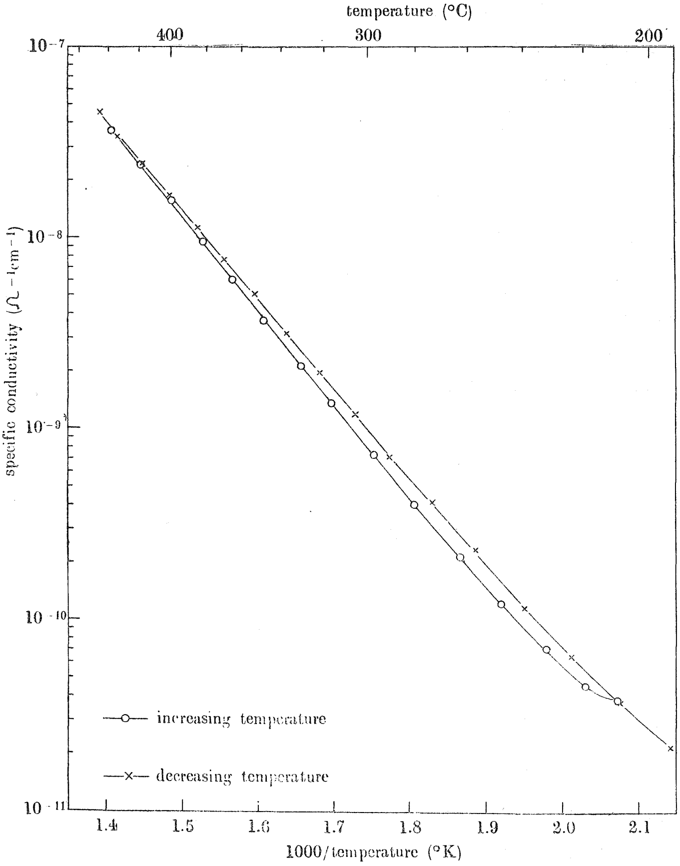


Fig. 5.—Temperature dependency of conductivity of a sample fired at 500°C for 4 hours.

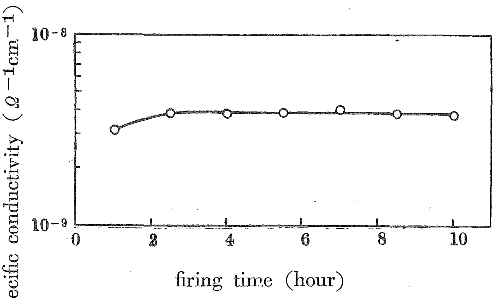


Fig. 6.—Change of conductivity (at 350°C) with firing time.

Next the samples fired for three hours at 500, 600, 800, 850, 900, 950, 1000, 1050, 1100, 1150 and 1200°C were made and the temperature dependencies of conductivity of them were measured. (That fired at 1300°C was exceedingly vitrified and it was impossible to measure the conductivity of it.) In Fig. 7, five examples of them are shown. Those of fired at 500°C and 600°C came to practically the same place as of 800°C. On the samples fired at more than 1000°C, the deviation from linearity was often observed. The curve of firing temperature of 1100°C in Fig. 7 is an example. As shall be referred to later, samples fired over 1000°C contains much cristobalite, the extraordinary expansion of which disturbs the electrode contact, which may be the cause of this irregularity.

The activation energies obtained from the slope of the lines are listed as follows:

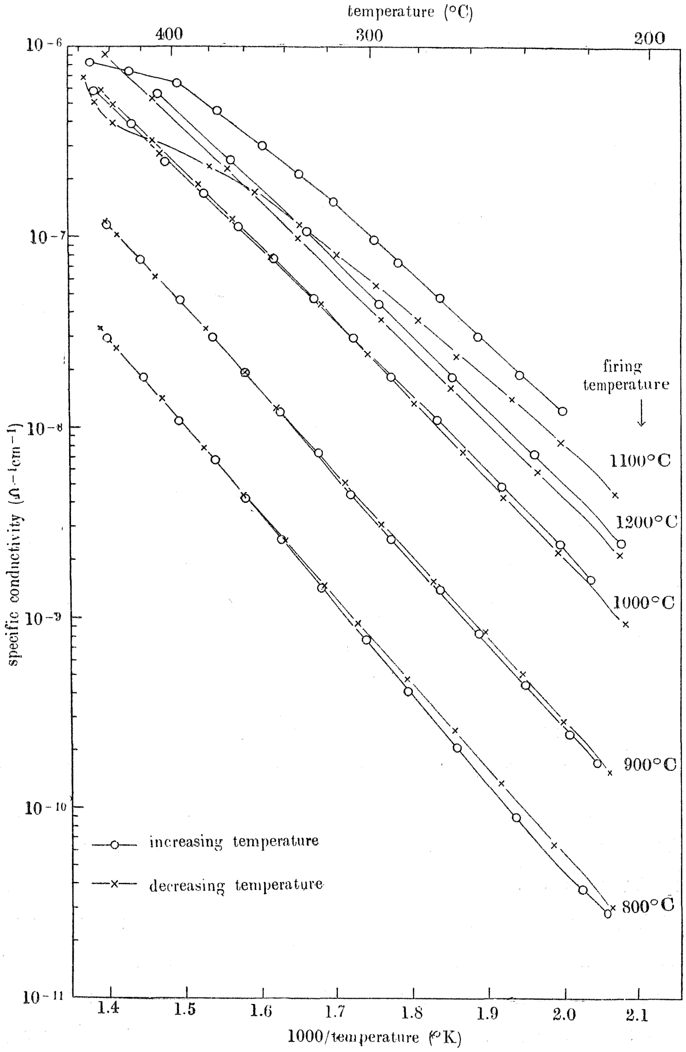


Fig. 7.—Temperature dependency of conductivity.

	Firing temperature	800	900	1000	1100	1200°C
ε	(increasing temperature)	1.1	1.1	0.9	0.8	0.9 eV
	(decreasing temperature)	1.1	1.0	0.9	0.9	0.9 〃

These seem to show the activation energy to decrease with firing temperature, but the change is not so decisive.

The change of conductivity with firing temperature is more distinct. To show it clearly, the conductivity at 250°C of each sample is presented in Fig. 8. The conductivities of samples fired at 500~800°C are alike, but for samples fired over 800°C, the conductivity increases with firing temperature, becomes maximum at about 1100°C, and decreases

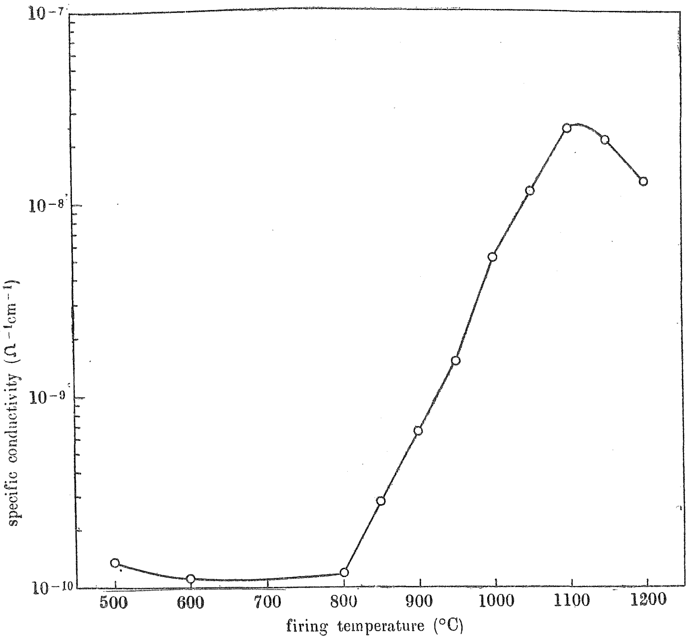


Fig. 8.—Change of conductivity (at 250°C) with firing temperature.

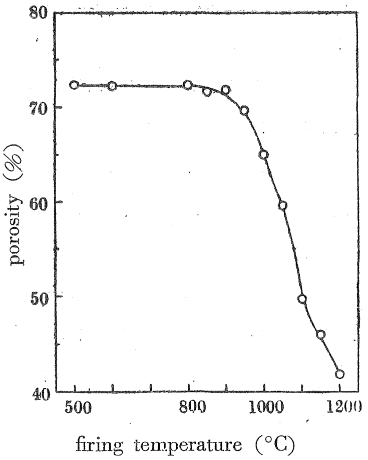


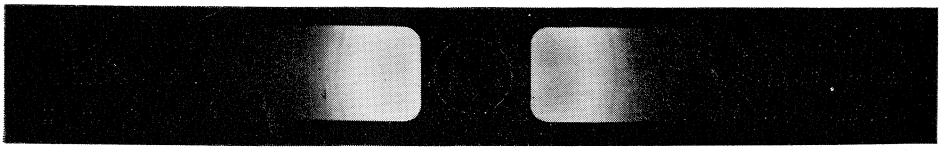
Fig. 9.—Change of porosity with firing temperature.

beyond there. On the other hand, the porosity of these samples was computed from the measurement of their bulk density and true density. It behaves as plotted in Fig. 9. It is also constant for 500~800°C, but it decreases monotonously beyond there without any extremum. Accordingly the increase of conductivity with firing temperature of 800~1100°C may be attributed to the decrease of porosity by sintering, but the decrease beyond there to another cause.

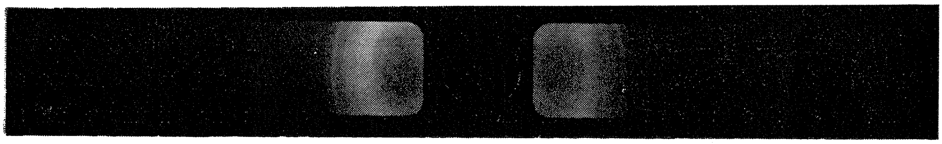
T. Nakai and Y. Fukami(5) examined the diatomaceous earth in the Island of Sado by means of X-ray method and measurement of true density, and reported that it was mainly amorphous under 800°C, crystallized slightly at 900°C, and became abundant in crystobalite with temperature of 1000~1400°C. Kawashima reported that the distinct diffraction lines were observed in the X-ray photograph of the diatomaceous earth from the Noto Peninsula fired at 1300°C, but not so distinct at 1000°C, and that the same conclusion was obtained from the measurement of thermal expansion(4) and true density.(1b)

Kawashima and Shiraki(1b) report that a small quantity of impurities contained in diatomaceous earth acts as a mineralizer and promotes the crystallization of amorphous sillica forming the frustules of diatoms. Therefore this transition temperature depends on the content of impurities.

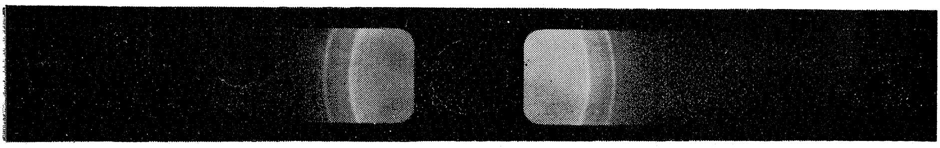
The present result of electrical conductivity to decrease with firing temperature over 1100°C seems to be attributed to this crystal transition. So the Debye-Scherrer photographs of those samples on which the conductivity had been measured were taken. These are shown in Fig. 10. There will be seen only very weak lines and diffraction halo for unfired sample and for one fired at 600°C, a few lines of crystobalite at 1000°C, and distinct lines of it at 1200°C. Therefore the change of concuctivity over



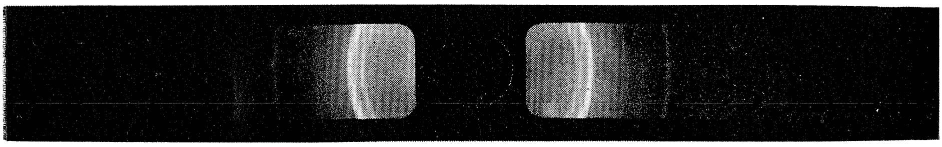
(a) unfired



(b) fired at 600°C



(c) fired at 1000°C



(d) fired at 1200°C

Fig. 10.—Powder diffraction patterns.

1100°C is due, partly at least, to the transition of the material to cristobalite. And this is consistent with the results of the previous authors.

§ 5. Summary

(1) The diatomaceous earths from Shôin of Suzu-shi were fired at 500°C for various hours, and the electric conductivity of them was measured. The samples fired for more than three hours showed a constant value.

(2) The activation energy computed from the temperature dependency of conductivity was about 0.9 eV.

(3) The temperature dependency of conductivity and the porosity of the samples fired at various temperatures of 500～1200°C were measured.

(4) Comparing the conductivities at a definite temperature of samples fired at various temperatures, it increases with firing temperature of 800～1100°C, and decreases over there. This result is consistent with the previous investigations of the transition to cristobalite at about 1100°C, and with the X-ray photographs of the present samples.

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