The Diffusion of Barium in a Rutile Single Crystal

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There have been many studies of diffusion in such solids as metals[1], metal halides[2,3] and metal oxides[4]. Little attention has, however, been paid, except in a few cases[5], to mutual diffusion between two metal oxides at higher temperature; this neglect has partly been due to the experimental difficulties and partly due to the chemical and/or crystallographic change taking place. We have studied the diffusion phenomena in the system of titanium dioxide and barium oxide in order to obtain some information concerning the chemical reaction of barium titanate formation and its sintering at higher temperatures. Our investigation is rather microscopic in nature, compared with the published reports of macroscopic observation[6,7]. In the present report, the change of state of the system is first observed qualitatively by means of an optical microscope. The diffusion of barium into a rutile single crystal is then measured by the radiotracer technique.

Experimental

Materials. — A rutile single crystal was obtained from the Tokyo Hoseki Co. The crystal was prepared by the flame fusion method[8] and was then annealed in oxygen gas at 1000°C[9]. Spectroscopic analysis revealed traces of silicon and iron as impurities. It seemed very likely that a minute amount of silicon would contaminate the rutile crystal, as it was ground in a mortar in the preparation of the spectroscopic specimens. Since the rutile crystal is optically anisotropic, the c-axis of the crystal was readily determined by a polarizing microscope. We obtained two kinds of rutile single-crystal plates by cutting, the one having a normal of the plate parallel to, and the other, one perpendicular to the c-axis. The direction of a normal of the crystal plate used for diffusion measurements was determined by X-ray Laue patterns. In most cases, the deviations of the X-ray resulting from the optical determination of the crystal axis were less than 2°. The barium carbonate powder for microscopic observations was of a Merk's reagent, the impurities being listed as calcium and alkali$<0.1\%$, iron$<0.001\%$, lead$<0.001\%$ and barium hydroxide$<0.03\%$. It was used without further purification. The barium carbonate used for the diffusion measurement was of a Johnson-Mathy's "specqure" grade, the impurities being listed as calcium 2 p. p. m., magnesium 1 p. p. m., and copper and sodium 1 p. p. m. Radioisotope ^{133}Ba was obtained as barium chloride in 1 N hydrochloric acid. It was mixed with the non-radioactive barium carbonate dissolved in hydrochloric acid. Sodium carbonate was then added to this mixture, and the labeled barium carbonate was obtained as a precipitate. The specific activity of the barium carbonate thus obtained was 4500 c.p.m./mg.

Microscopic Observations. — As it was difficult to observe a cross-section of the contact plane between the rutile single crystal and the barium carbonate powder, the barium carbonate powder was placed

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[1] D. Lazarus, "Solid State Physics", Vol. 10, Academic Press, New York (1960).

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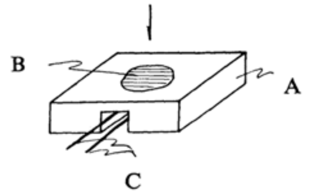

Fig. 1. Microscopic observation of diffusion system at high temperature.
A Rutile single crystal
B Powder of barium carbonate
C Thermocouple
Arrow shows the direction of the observation.

on the rutile crystal and the changes of the state were observed from above at a high reaction temperature, as is shown in Fig. 1. The temperature of the system was measured by inserting a Pt/Pt-Rh hot-junction (C in Fig. 1) into the rutile single crystal. It was reported that rutile is reduced when it is heated in vacuo ($10^{-5}\sim10^{-4}$ mmHg) at a high temperature[10]. Therefore, the phenomenon we observed was the phase change of the system consisting of a single crystal of rutile with small oxygen vacancies and the powder of barium carbonate at a high temperature. However, as we kept the system at a high temperature for rather a short time (30 to 60 min.), such a reduction of rutile, if any, seemed not to influence the results obtained. After allowing the diffusion to take place at a high temperature (1100~1400°C) for two hours in oxygen gas to avoid reduction, it was cooled; the cross-section of the diffusion layer was then observed at room temperature. To enlarge the cross-section of the reaction layer, the sample plate was cut out obliquely, as may be seen in Fig. 2.

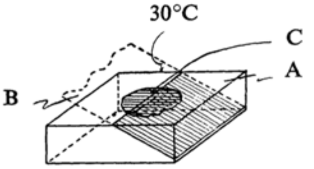

Fig. 2. Cross section of diffusion layer for microscopic observation.
A Rutile single crystal B Cross-section
C Reacted area

Measurement of the Diffusion Coefficient of Barium.—For the diffusion experiment at a high temperature, oxygen gas was led into the furnace at the rate of 2~3 l./hr. under 1 atm. to avoid the back reaction of the carbon dioxide and barium oxide produced by the decomposition of barium carbonate forming barium carbonate again, and to prevent the reduction of rutile at the high temperature. Prior to the introduction of oxygen, the furnace was evacuated by a vacuum pump. The rate-controlled oxygen gas was then passed through a heated platinum black to change the hydrogen impurity into water, which was then cooled and removed by a potassium hydroxide solution and silica gel. The carbon dioxide in the oxygen was also removed by means of an alkaline solution. As is shown in detail in Fig. 3, the oxygen current was preheated before it reached the diffusion system. The rutile crystal sample was cut to about $10\times10\times1$ mm., and a few milligrams of ^{133}Ba-labeled barium carbonate powder were put on the crystal. The whole system was mounted on the ceramic boat, A, and was heated to a desired temperature under the oxygen current. The Pt/Pt-Rh thermocouple was set outside the alumina sheath, C, close to the sample. The actual temperature of the sample inside the alumina sheath was 5°C lower than the value indicated by the thermocouple.

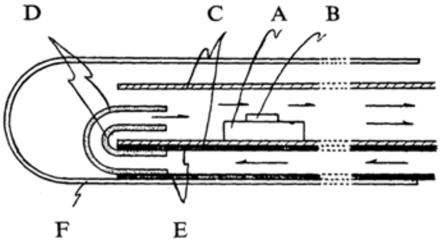

Fig. 3. Sketch of sample mounting in the muffle tube.
A Ceramic boat B Sample
C Alumina sheath D Fused-quartz pipe
E Preheating gas guide tube
F Muffle tube
Arrow shows the direction of gas flow.

After the radioactive material had been heated, utmost care was taken of the waste gas, which was passed through concentrated sulfuric acid and through glass fiber filters to catch the radioactive barium oxide. Actually, however, the radioactivity was not detectable in either the sulfuric acid or in the filters. After the barium had diffused into a single crystal of rutile at a high temperature, the surface of the specimen was abraded successively with powder of carborundum, keeping it flat; the decrement of the thickness was measured by an electromicrometer, the precision of which was checked with a block-gauge to be $0.2\,\mu$/div. The residual radioactivity of the abraded surface due to ^{133}Ba diffusion was measured by a G-M counter. The G-M tube used was equipped with a mica window 27 mm. in diameter and 3.4 mg./cm^2 thick. The specimen was placed 32 mm. below the window. To avoid the edge effect of the diffusion area, we masked the surface of the specimen with a lead plate (12 mm. thick) which had a circular hole 3 mm. in diameter in its center, through which the γ-radiation of ^{133}Ba (half life: 7.2 years) free from self-absorption was measured.

Results and Discussion

Microscopic Observations.—Two processes of diffusion can occur when a single crystal of rutile is in contact with barium oxide at a high temperature, namely: the diffusion of barium into the rutile crystal, the diffusion layer being formed inside the rutile crystal, and the

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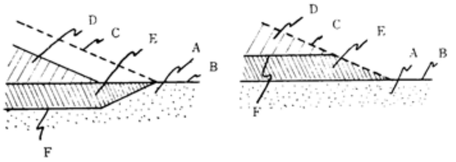
[10] M. E. Straumanis et al., *Acta Cryst.*, 14, 493 (1961).

diffusion of titanium into barium oxide, the diffusion layer being formed outside the single crystal of rutile. The two processes are illustrated in Figs. 4 (a) and (b) respectively, assuming that the volume does not change on diffusion. To confirm which process really happened, the diffusion layer was cut as shown in Fig. 2 after diffusion had taken place at a high temperature (1300°C, 1 hr.) and was then observed by a microscope (Fig. 5). In this specimen, the c-axis of the rutile crystal was at right angles to the diffusion layer. In Fig. 6, the diffusion front, F, was seen to advance across the reference plane, B, into the rutile crystal region. Therefore, it is clear that barium diffused into the rutile crystal and that the diffusion phenomenon observed was the case of Fig. 5 (a). The diffusion layer was seen to be polycrystalline, and observation by a polarization microscope showed that the optical anisotropy of the crystal grains was random in its direction. This suggests that the crystal grains of the diffusion product did not grow epitaxially. It is likely for the diffusion mechanism that barium diffuses into the rutile single crystal, destroys the crystal structure of rutile, and creates a new crystal structure consisting of titanium, barium and oxygen. A sufficient number of new crystal nuclei are created to result in the polycrystalline diffusion layer.



(a) (b)

Fig. 4. Diffusion layer model. (a) is the case where barium diffuses into the rutile single crystal, and (b) titanium diffuses into barium oxide.

A Rutile single crystal
B Surface of rutile
C Barium oxide before diffusion
D Residual barium oxide after diffusion
E Diffusion layer F Diffusion front

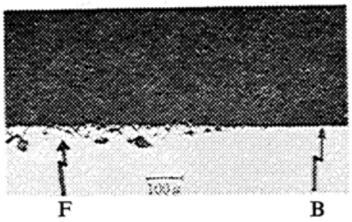
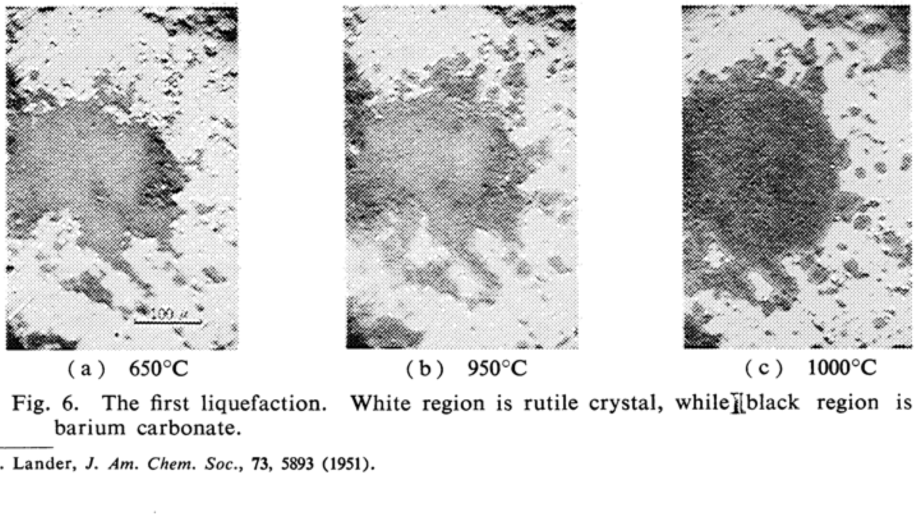


Fig. 5. Microphotograph of the cross-section of diffusion layer. B shows rutile crystal surface, white region being rutile crystal. F is diffusion front.

Since the diffusion of an atom is considered to take place more rapidly in the liquid state than in the solid state, the rate of reaction is expected to be affected profoundly by the liquefaction of the diffusion layer. Microscopic observation of the diffusion system of Fig. 1 at a high temperature revealed two kinds of liquid state. The first liquefaction occurred at 900∼1050°C. At the lower temperature of 650°C, the barium carbonate in the single crystal of rutile seemed to remain in a solid state, as is shown in Fig. 6 (a). It was liquefied at 950°C, as is shown in Fig. 6 (b). The fluidity was seemingly increased at 1000°C, as is indicated in Fig. 6 (c). The accuracy of the temperature measurement depended on the position of the hot-junction placed beneath the rutile crystal, as may be understood from Fig. 1. The accuracy of the temperature measurement was ±25°C. Accordingly, the liquid state is considered to be a eutectic mixture of $2BaCO_3 \cdot BaO$, the eutectic point of which is 1030±3°C[11]. This liquid



(a) 650°C (b) 950°C (c) 1000°C

Fig. 6. The first liquefaction. White region is rutile crystal, while black region is barium carbonate.

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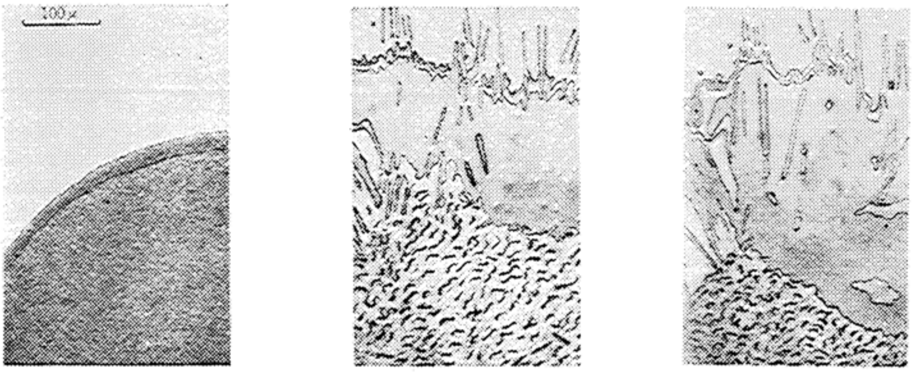
[11] J. J. Lander, *J. Am. Chem. Soc.*, 73, 5893 (1951).



(a) 1200°C (b) 1290°C (c) 1300°C

Fig. 7. The second liquefaction. White region is rutile crystal, while black region is barium carbonate.
Lines are drawn to emphasize the contours and the details of the figures.

state can also be identified with the one observed by Hirota et al.[12], who studied the thermal decomposition of barium carbonate with an electron microscope. Therefore, the liquefaction in the temperature range of 900~1050°C may be considered to be related to barium carbonate and oxide, which may affect the diffusion of barium into a rutile crystal very little.

The second liquefaction occurs at about 1300°C. This is shown in Fig. 7(c). As will be mentioned later, this liquefaction is exclusively concerned with barium oxide and titanium dioxide, not with barium carbonate. To confirm this, barium oxide film was made by evaporation in vacuo on a single crystal of rutile, and barium was diffused into the rutile crystal at a high temperature in vacuo ($5\sim7\times10^{-5}$ mmHg). At 1200°C (Fig. 7 (a)) no liquid state was observed, but at 1290°C (Fig. 7 (b)) the liquefaction was recognized from the interference fringes caused by a relatively uniform liquid film. According to the phase diagram of barium oxide~titanium dioxide proposed by Rose and Rey[6], a eutectic mixture exists at the mole ratio of $BaO:TiO_2$ 68 : 32 (eutectic point 1317°C). Therefore, the liquid phase observed is considered to be the eutectic mixture of this composition produced by the diffusion of barium. This liquefaction explains the marked change in reaction velocity, namely, above 1317°C barium diffusion is rapid, since it takes place in the liquid state, while below 1317°C it is rather slow, owing to the solid state diffusion. This is confirmed further by the following quantitative experiment.

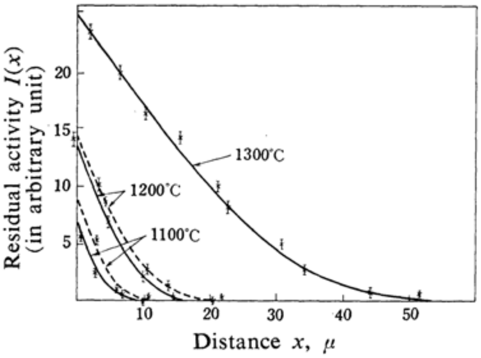


Fig. 8. Relation between diffusion distance and residual activity $I(x)$.
—— Diffusion parallel to c-axis of rutile single crystal
---- Diffusion perpendicular to c-axis of rutile single crystal

Radiotracer Observation.—After the diffusion was allowed to take place at high temperatures, the reacted surface was abraded by successive thin layers. After each abrasion the residual radioactivity of the surface was measured. Figure 8 shows the residual radioactivity curve $I(x)$, denoting, in an arbitrary unit, the concentration of barium remaining after the abrasion to the depth x, measured from the plane of contact between the rutile single crystal and ^{133}Ba carbonate. Then, we obtain:

$$I(x)=\int_x^{\infty} c(x')\cdot A(x'-x)\,\mathrm{d}x' \qquad (1)$$

where $A(x'-x)$ is the factor due to the self-absorption of radioactivity through the reacted rutile crystal of the thickness of $x'-x$, and $c(x')$ is the barium concentration per unit thickness at x' for $x'\geqq x$. Differentiating with respect to x, we get

$$\begin{aligned}\mathrm{d}I(x)/\mathrm{d}x&=[-c(x')\cdot A(x'-x)]_{x'=x}\\&=-c(x)\cdot A(0)\end{aligned} \qquad (2)$$

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[12] S. Hirota et al., *J. Phys. Soc.* (*Japan*), **15**, 137 (1960).

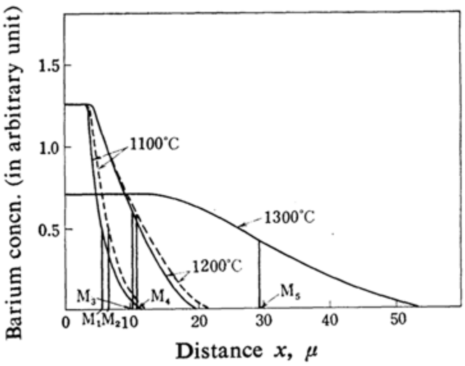

Fig. 9. Relation between diffusion distance and barium concentration $c(x)$.
—— Diffusion parallel to c-axis of rutile single crystal
---- Diffusion perpendicular to c-axis of rutile single crystal

However, since

$$A(0)=1$$

Equation 2 becomes

$$\mathrm{d}I(x)/\mathrm{d}x=-c(x) \tag{3}$$

That is, the barium concentration $c(x)$ is given by the negative of the tangent of $I(x)$.

Figure 8 shows the diffusion systems of barium carbonate on the rutile single crystal, systems which were heated to 1100, 1200 and 1300°C under the oxygen current for two hours. As the ionic configuration along the c-axis of the rutile is quite different from that perpendicular to the c-axis[9], the $I(x)$'s along both directions were determined. We can see in Fig. 8 that barium diffuses more rapidly at 1300°C than at 1100 and 1200°C, which may be explained by the formation of liquefied eutectic mixture at 1300°C mentioned above. The $c(x)$ curves in Fig. 9 were obtained by the differentiations of the curves of Fig. 8. Small differences are seen between the $c(x)$ curves parallel to and those perpendicular to the c-axis, but the anisotropic diffusion of barium is not conclusive from these data alone. Above 1300°C, liquefaction occurred and the volume of the diffusion layer slightly decreased, so that the accuracy of $I(x)$ beyond 1300°C is rather low. Actually, no quantitative result could be obtained at 1400°C.

For the calculation of the diffusion coefficient from the concentrations distribution curve, initial and boundary conditions should be given; in our experiments these were:

$$\begin{aligned} c(x)&=\text{const.} \quad \text{for } x<0, \quad t=0 \\ c(x)&=0, \quad\quad\;\; \text{for } x>0, \quad t=0 \end{aligned} \tag{4}$$

where t denotes time.

As a diffusion coefficient is assumed to be dependent on the concentration, the diffusion equation takes the form:

$$\frac{\partial c}{\partial t}=\frac{\partial}{\partial x}\left(D(c)\cdot\frac{\partial c}{\partial x}\right) \tag{5}$$

Using the Matano interface[14], $D(c)$ can be calculated readily under the conditions of 4. Let c_M be the concentration on the Matano interface, then the diffusion coefficient at c_M is[13]:

$$D(c_M)=-\frac{1}{2t}\left(\frac{\mathrm{d}x}{\mathrm{d}c}\right)_{c=c_M}\cdot\int_0^{c_M}x\mathrm{d}c \tag{6}$$

The Matano interfaces $M_1, M_2, M_3, \ldots, M_5$ are shown in Fig. 9 for each concentration curve. $D(c_M)$ was calculated using Eq. 6.

The values of $D(c_M)$ obtained were 3.6×10^{-14} (1100°C) and 1×10^{-13} (1200°C) (both parallel to the c-axis), 5×10^{-14} (1100°C) and 2.4×10^{-13} (1200°C) (both perpendicular to the c-axis), and 2.5×10^{-12} (1300°C), expressed in $\mathrm{cm}^2/\mathrm{sec}$. As for the self-diffusion coefficient of barium in barium titanate, Verduch and Linder[14] gave about $10^{-14}\ \mathrm{cm}^2/\mathrm{sec}$. at 1150°C, which is in reasonable agreement with our result of about $3\times10^{-14}\ \mathrm{cm}^2/\mathrm{sec}$. at 1100°C.

Assuming that the activation energy, E, for diffusion is independent of the temperature, T, it can be calculated from:

$$D(c_M)=D_0(c_M)\cdot\exp\left(-E/\boldsymbol{R}T\right)$$

by plotting $D(c_M)$ against $1/T$. The rough estimation of E in the of 1100~1200°C range gives 59 kcal./mol. (perpendicular to the c-axis) and 43 kcal./mol. (parallel to the c-axis).

With regard to the state of barium during diffusion, no conclusive statement can be made from our results. However, the experimental results of barium self-diffusion in barium oxide by Redington[15] show, that both charged and neutral barium constituents diffuse in the temperature range from 1077 to 1227°C, whereas only the neutral barium diffuses in the lower temperature range (327~1027°C). Thus we may expect that the barium diffusing in our experiments (1100°C and above) is partly charged and partly neutral.

In these experiments, the average concentration was determined over a circular area 3 mm. in diameter, assuming that the diffusion proceeds vertically to the rutile surface and that the diffusion front is flat. Actually, however, as is shown in Fig. 5, the photomicrograph reveals, that the diffusion front is not completely flat over the area observed. In addition,

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[13] Cf., for instance, J. Crank, "The Mathematics of Diffusion", Oxford Univ. Press, London (1956).

[14] A. G. Verduch and R. Linder, "Proc., Intern. Symposium on Reactivity of Solids, Gothenberg, 1952", (1954), p. 207.

[15] R. W. Redington, *Phys. Rev.*, **87**, 1066 (1952).

barium is considered to diffuse rather rapidly along such imperfections of the rutile single crystal as the subgrain boundaries. It may be possible to obtain a more exact concentration curve without being disturbed by crystal imperfections if the diffusion is studied by the X-ray microanalyzer. The chemical composition and the crystal structure may also be identified by the X-ray microanalyzer and microdiffraction methods. The details, however, require further study.

Summary

1) Microscopic and radiotracer studies have been made upon the diffusion of barium into a rutile single crystal.

2) In the microscopic observation, the diffusion layer of barium oxide in the rutile single crystal was confirmed to liquefy above 1300°C due to the formation of a eutectic mixture between both constituents. Below 1300°C solid phase diffusion prevails, and the diffusion layer consists of polycrystalline of a random orientation.

3) The diffusion coefficients of barium oxide in a rutile single crystal were measured by means of the radiotracer method using ^{133}Ba. The diffusion coefficients obtained were $3.5\times10^{-14}\sim2.4\times10^{-13}$ cm^2/sec. in the range of 1100∼1200°C and 1.1×10^{-12} cm^2/sec. at 1300°C. Between 1100°C and 1200°C, small differences seemed to be observed for the values obtained according to the direction of the diffusion in the crystal, but this is not conclusive. The large value of the diffusion coefficient at 1300°C was considered to be due to the liquefaction of the diffusion layer. The energy of activation was calculated to be 43 kcal./mol. (parallel to the c-axis) and 59 kcal./mol. (perpendicular to the c-axis).

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