BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN　VOL. 40　843—851 (1967)

Some Aspects of Solid State Reactions between Oxides

Goro YAMAGUCHI and Toshio TOKUDA

Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Tokyo

(Received September 16, 1966)

Solid state reactions in air between two oxide pieces of a single crystal or a polycrystal were conducted and observed; the couples were MgO and Al_2O_3, ZnO and Al_2O_3, MgO and Fe_2O_3, MgO and Cr_2O_3, MgO and SiO_2, MgO and TiO_2, and CoO and TiO_2. In all the reactions except the MgO-Fe_2O_3 reaction, the two pieces were easily separated after the reaction. Moreover, in all the reactions except the MgO-SiO_2 reaction, the reacted substances adhered selectively to one of those two pieces. The host crystals (to which the reacted substances adhered) were Al_2O_3 in the cases of MgO-Al_2O_3 and ZnO-Al_2O_3, Fe_2O_3 in the case of MgO-Fe_2O_3, MgO in the case of MgO-Cr_2O_3, and TiO_2 in the cases of MgO-TiO_2 and CoO-TiO_2. In the reaction between MgO and SiO_2, $2MgO\cdot SiO_2$ adhered to MgO and $MgO\cdot SiO_2$ adhered to SiO_2. In the reactions of MgO-TiO_2 and CoO-TiO_2, three layers of different compounds were formed, all adhering to TiO_2. The mechanism of the diffusion of ions through the reacted layer was hard to determine in detail. It was pointed that the investigators must be careful in confirming the field of diffusion and in discriminating the diffusion through the diffusion field of the lattice from that through the surface and the space. Only in the cases of MgO-Al_2O_3 and ZnO-Al_2O_3 was the mechanism clearly determined to be the counter diffusion of cations through the spinel lattice formed, by means of a natural mark.

A clarification of the material transport in the solid state reaction is the most important step in systematizing the kinetics of such reactions. Many investigators have reported phenomena in the solid state reactions; some reports are coincident with another, but others are inconsistent. Therefore, it is now necessary to reexamine many reactions and find out their common features.

Experimental

Specimens. *MgO Single Crystal.* A single crystal from fused magnesia was cut along an a(100) plane to make a reaction face.

MgO Polycrystal. Pure magnesium oxide powder was pressed into a pellet and sintered at 1500°C for 2 hr.

Al_2O_3 Single Crystal. A synthetic sapphire was cut along a c(0001) plane to make a reaction face.

ZnO Polycrystal. Pure zinc oxide powder was pressed into a pellet and sintered at 1300°C for 2 hr.

Cr_2O_3 Polycrystal. Pure chromic oxide powder was pressed into a pellet and sintered at 1300°C for 2 hr.

TiO_2 Single Crystal. A synthetic rutile bole was cut along an a(100) plane to make a reaction face.

CoO Polycrystal. Pure cobaltous oxide powder was pressed into a pellet and sintered at 1200°C for 2 hr.

SiO_2 Polycrystal. Pure silica gel powder was pressed into a pellet and sintered at 1550°C for 3 hr. After the sintering, the gel was recognized to have been inverted into cristobalite.

Fe_2O_3 Polycrystal. Pure ferric oxide powder was pressed into a pellet and sintered at 1100°C for 2 hr.

All the specimens were cut into pieces about 0.5 cm square and 0.2 cm thick. The reaction faces of all the pieces were polished with diamond paste.

Reaction Procedure. Polished faces of two kinds of specimen pieces were placed so as to touch closely. Then the two specimens were wrapped in a platinum foil and heated in an automatically-temperature-regulated electric furnace for a certain period. After the reaction period, the electric furnace was cooled and the specimens were taken out.

Analytical Method. Pieces of specimens were tested according to the following methods.

X-Ray Analysis. The X-ray diffraction analysis by means of the Back-Laue method and the powder method were performed on the reacted surface if a reacted substance had to be confirmed.

Microscopic Observation. The specimen pieces were cut into sections perpendicular to the reaction faces and polished. The sections were microscopically tested by transmitting light in the case of a transparent specimen and by reflecting light in the case of an opaque specimen.

Electron-probe Micro Analysis. A polished specimen piece for the microscopic observation was coated with a carbon film. The process of carbon coating was as follows; a carbon film made by spattering upon a cleavage plane of a mica crystal was separated from the plane and floated on the water, and then scooped up and settled on a polished face of a specimen piece. On the carbon-coated face an electron beam was scanned perpendicularly to the reaction interface. In order to estimate the quantities of certain components, a standard sample synthesized in a definite composition was applied to calibration.

Results

Reaction in the MgO-Al_2O_3 (MgO Single Crystal - Al_2O_3 Single Crystal) System. In this system only a spinel, $MgO\cdot Al_2O_3$, has been recognized as a compound. It is also known that

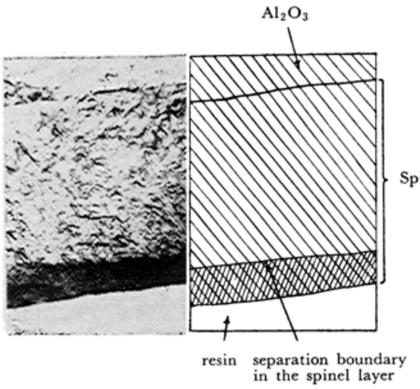

Fig. 1. Section perpendicular to the reaction surface of a sapphire piece reacted with a polycrystalline MgO piece at 1500°C for 70 hr. (×300)

an excess of Al_2O_3 is dissolved into $MgO\cdot Al_2O_3$ as a solid solution.[1] After a reaction at 1500°C for 70 hr, the pair easily separated into two pieces. On the reaction face of the MgO piece there existed no reacted substance; only on the reacted face of the Al_2O_3 did there exist a spinel layer about 200 μ thick, as is shown in Fig. 1. The spinel layer closely adhered to the Al_2O_3 piece. Figure 1 shows that the spinel layer consists of two kinds of textures. The ratio of the thickness of the outside (the MgO side) texture to that of the inside (the Al_2O_3 side) texture is about 1 to 4.5. A Back-Laue X-ray examination showed that the inside spinel texture had a fairly good orientation in many cases, while the outside one was oriented rather randomly. The electron-probe microanalysis revealed that the spinel layer had a concentration gradient, as is shown in Fig. 2. From this finding it seems that the composition of the spinel is almost $MgO\cdot Al_2O_3$ at a contact fact with MgO, while it is nearly $MgO\cdot 1.5Al_2O_3$ at a contact face with Al_2O_3.

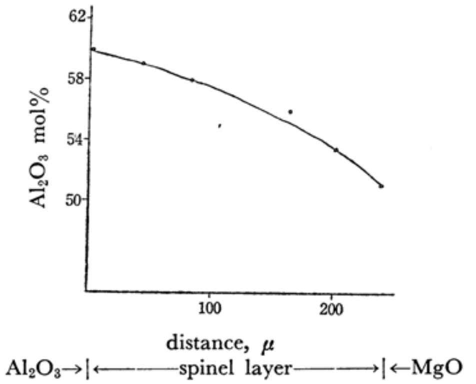

Fig. 2. Al_2O_3 concentration profile in the $MgO\cdot Al_2O_3$ layer in Fig. 1 determined by electron microprobe analysis.

Reaction in the ZnO-Al_2O_3 (ZnO Polycrystal-Al_2O_3 Single Crystal) System. In this system only a spinel, $ZnO\cdot Al_2O_3$, has been recognized as a compound, and no distinct solid solubility is found.[2] After a reaction at 1500°C for 70 hr (as ZnO was very volatile, a few pieces of ZnO had to be replaced during the reaction), the pair easily separated into two pieces. On the reaction face of the ZnO piece there existed no reacted substance; only on the reacted face of the Al_2O_3 did there exist a spinel layer, about 180 μ thick, as is shown in Fig. 3. The spinel layer closely adhered to the Al_2O_3 piece. Figure 3 shows that the spinel layer consists of two kinds of textures. The ratio of the thickness of the outside (the ZnO side) texture to that of the inside (the Al_2O_3 side) texture is about 1 to 3. The results of a Back-Laue X-ray examination was almost the same as with the $MgO\cdot Al_2O_3$ formation. Moreover, as a result of the electron probe microanalysis no distinct solid solution could be seen.

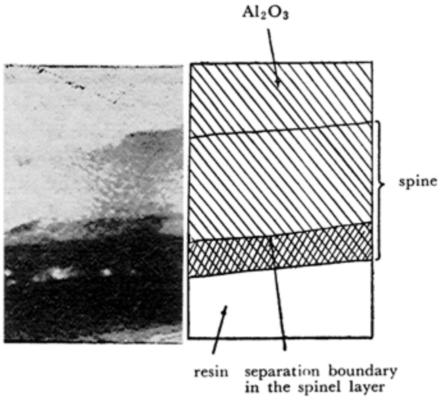

Fig. 3. Section perpendicular to the reaction surface of a sapphire piece reacted with a polycrystalline zinc oxide piece at 1500°C for 70 hr. (×250)

Reaction in the MgO-Fe_2O_3 (MgO Polycrystal - Fe_2O_3 Polycrystal and MgO Single Crystal - Fe_2O_3 Polycrystal) System. In this system only a spinel, $MgO\cdot Fe_2O_3$, has been recognized as a compound, but at high temperatures Fe_2O_3 is reduced and forms MgO-type solid solutions.[3]

(a) Reaction between the MgO Polycrystal and the Fe_2O_3 Polycrystal at 1250°C for 70 hr. After the reaction the two pieces were adhering closely and could not be separated. A section is shown in Fig. 4. In appearance the original MgO piece is eroded by the swelling of the Fe_2O_3 piece. Figure

---

[1] A. M. Alper and R. N. McNally, *J. Am. Ceram. Soc.,* **45,** 264 (1962).

[2] E. N. Bunting, *Bur. Standards J. Research,* **8,** 280 (1962).

[3] B. Phillips, S. Somiya and A. Muan, *J. Am. Ceram. Soc.,* **44,** 169 (1961).

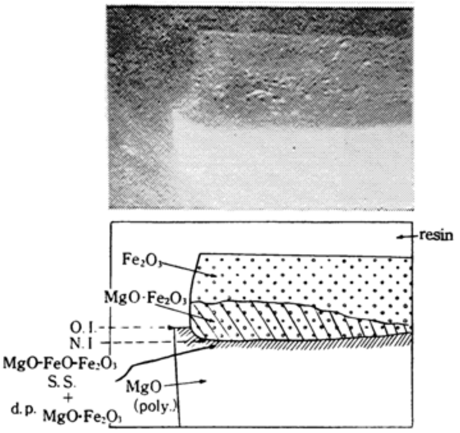

Fig. 4. Section of a MgO(poly)-Fe_2O_3 couple fired at 1250°C for 70 hr. (×40)
O.I.=original interface
N.I.=new interface
S.S.=solid solution
d.p.=deposited during cooling

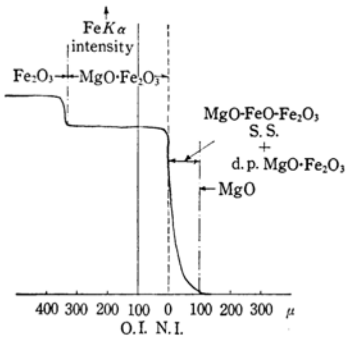

Fig. 5. Electron microprobe scanning figure as drawn perpendicular to the interface of the section in Fig. 4.
O.I.=original interface
N.I.=new interface
S.S.=solid solution
d.p.=deposited during cooling
E.P.M.A. conditions (Fe$K\alpha$)

accerating voltage	25 K.V.	absorption current	0.29μA
analyzing crystal	quartz	gain	8
scanning speed	20μ/min		

5 is a scanning figure of the electron-probe microanalysis; it is assumed that the reacted and swelling part on the Fe_2O_3 is a spinel, $MgO \cdot Fe_2O_3$, phase and that there exists an MgO-type solid solution of the MgO-FeO-Fe_2O_3 system with a concentration gradient on the MgO side. However, the X-ray powder diffraction examinations showed there was also a small amount of spinel in this seeming MgO-FeO-Fe_2O_3 solid solution. Nevertheless, considering the MgO-Fe_2O_3 phase diagram in air,³⁾ the spinel seems to have been segregated from the solid solution during cooling.

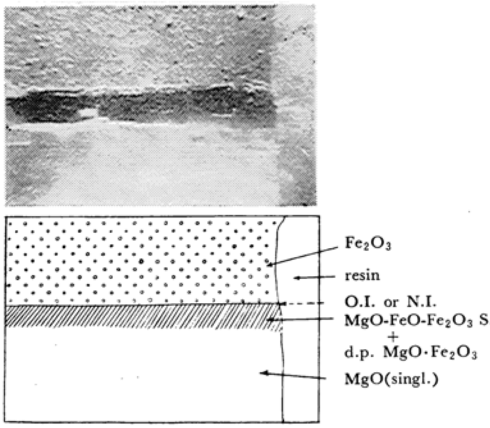

Fig. 6. Section of a MgO(singl.)-Fe_2O_3 couple fired at 1250°C for 70 hr. (×40)
O.I.=original interface
N.I.=new interface
S.S.=solid solution
d.p.=deposited during cooling

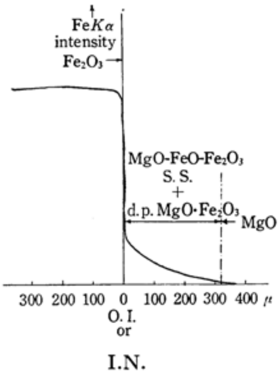

Fig. 7. Electron microprobe scanning figure as drawn perpendicular to the interface of the section in Fig. 6.
O.I.=original interface
N.I.=new interface
S.S.=solid solution
d.p.=deposited during cooling
E.P.M.A. conditions same as in Fig. 5.

(b) Reaction between the MgO Single Crystal and the Fe_2O_3 Polycrystal at 1250°C for 70 hr. After this reaction also the two pieces were adhering closely and could not be separated. A section is shown in Fig. 6. In this case no appreciable change in the interface of the two pieces has taken place except that a reddish brown layer has been formed on the MgO side. Figure 7 is a scanning figure of the electron-probe microanalysis; it has been found that the reddish-brown layer is probably an MgO-type MgO-FeO-Fe_2O_3 with a small amount of segregated spinel, and that no spinel formation has taken place on the Fe_2O_3 side.

(c) Reaction between the MgO Single Crystal and the Fe_2O_3 Polycrystal at 1400°C for 20 hr. In this

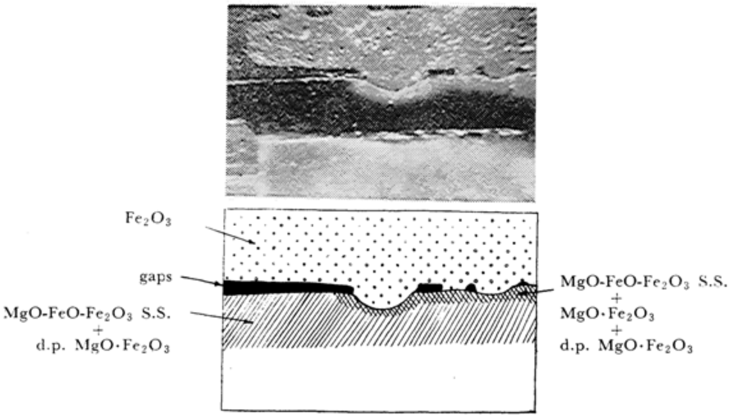

Fig. 8. Section of a MgO(singl.)-Fe_2O_3 couple fired at 1400°C for 20 hr. (×40)
O.I. = original interface N.I. = new interface
S.S. = solid solution d.p. = deposited during cooling

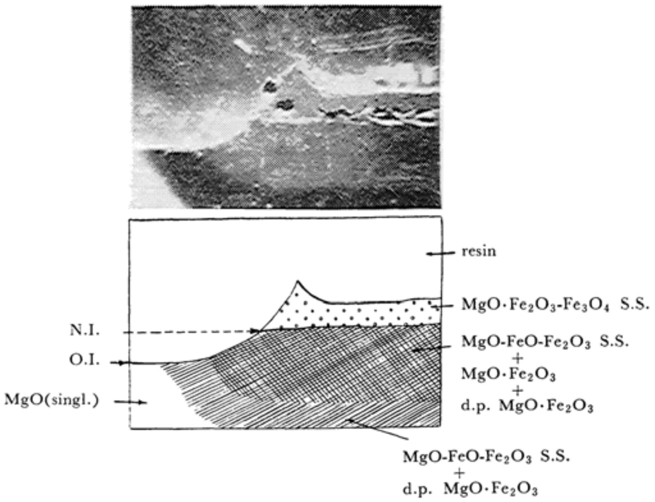

Fig. 9. Section of a MgO(singl.)-Fe_2O_3 couple fired at 1500°C for 20 hr. (×40)
O.I. = original interface N.I. = new interface
S.S. = solid solution d.p. = deposited during cooling

case the phenomena resemble the case (b), but, as Fig. 8 shows, the original Fe_2O_3 piece has locally swelled into the MgO single crystal piece, forming a spinel.

(d) Reaction between the MgO Polycrystal and the Fe_2O_3 Polycrystal and that between the MgO Single Crystal and the Fe_2O_3 Polycrystal at 1500°C for 20 hr. The phenomena in those two cases were almost the same. After the reaction the two pieces adhered closely and could not be separated. A section is shown in Fig. 9. In this case, contrary to the case (a), the original Fe_2O_3 piece seems to be eroded by the swelling of the MgO piece. It is observed microscopically that two colored layers exist in the reacted and swelled parts of the MgO piece. One is yellowish brown and near the Fe_2O_3 side, while the other is reddish brown and is farther from that side. These two layers were analyzed by the X-ray method; it was thus clarified that both consisted of spinel and MgO-type solid solutions. The difference in color may be due to the difference in the amount of spinel present in them. Figure 10 is a scanning figure of the electron-probe microanalysis. The eroded Fe_2O_3 side seemed to contain no reacted layer, but it was clarified by the use of the X-ray method that the contact layer contained a spinel phase.

Reaction in the MgO-Cr_2O_3 (MgO Single Crystal - Cr_2O_3 Polycrystal) System. In this system only a spinel, MgO·Cr_2O_3, has been recognized as a compound; a fairly large solid solubility of Cr_2O_3 into MgO is also recognized.[4] After a reaction at 1400°C for 24 hr, the pair easily

---

[4] A. M. Alper, R. N. McNally, R. C. Doman and F. G. Keihn, *ibid.*, **47**, 30 (1964).

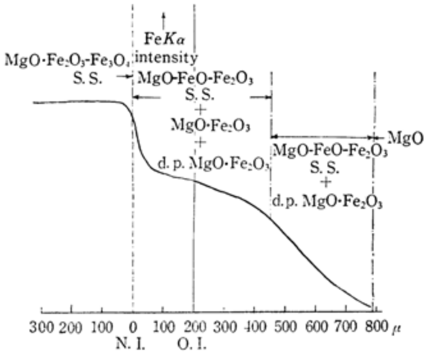

Fig. 10. Electron microprobe scanning figure as drawn perpendicular to the interface of the section in Fig. 9.
O.I. = original interface
N.I. = new interface
S.S. = solid solution
d.p. = deposited during cooling

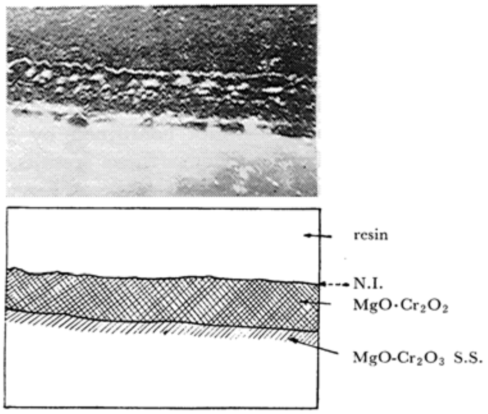

Fig. 11. Section perpendicular to the reaction face of a MgO(singl.) piece reacted with a Cr_2O_3(poly.) piece at 1400°C for 20 hr. (×40)
N.I. = new interface S.S. = solid solution

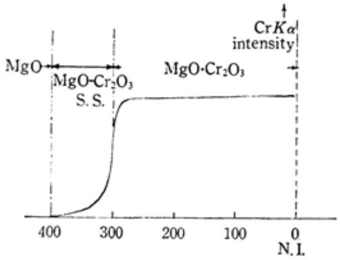

Fig. 12. Electron microprobe scanning figure as drawn perpendicular to the interface of the section in Fig. 11.
N.I. = new interface S.S. = solid solution
E.P.M.A. conditions (CrKα) same as in Fig. 5.

separated into two pieces. On the reaction face of the Cr_2O_3 piece there existed no reacted substance; only on the reaction face of the MgO piece did there exist a spinel layer, about 400 μ thick. The spinel layer adhered closely to the MgO piece. A Back-Laue photograph of the spinel layer showed a good orientation, with an oxygen packing succeeding to that of the host crystal. A section is shown in Fig. 11, which shows that there exists a spinel layer and also a solid solution layer of $MgO-Cr_2O_3$ ahead of the spinel layer. This fact was confirmed by the electron-probe microanalysis, as is shown in Fig. 12. In this case, and also in the case of $MgO-Fe_2O_3$, a double-layer texture of a spinel layer, as in the cases of $MgO\cdot Al_2O_3$ and $ZnO\cdot Al_2O_3$, was not clear.

Reaction in the $MgO-SiO_2$ (MgO Polycrystal-SiO_2 Polycrystal) System. In this system two compounds, forsterite $2MgO\cdot SiO_2$ and enstatite $MgO\cdot SiO_2$, are dominant.[5] After a reaction at 1500°C for 70 hr, the pair was easily separated into two pieces. The reacted faces were analyzed by the X-ray powder method, it was thus clarified that clino- or proto-enstatite was formed on the reaction face of the SiO_2 piece, while on the reaction face of the MgO piece, as Fig. 13 and Fig. 14 show. Figure 15 shows the results of the electron-probe microanalysis; there is a forsterite layer about 15 μ thick in the MgO piece and an enstatite layer about 30 μ thick in the SiO_2 piece.

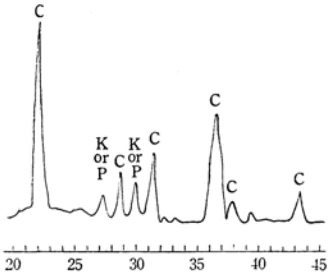

Fig. 13. X-Ray powder diffraction pattern of the surface of a SiO_2(poly.) piece reacted with a MgO(singl.) piece at 1500°C for 70 hr. (CuKα, 40 kV., 10 mA)
C = cristobalite K = klino-enstatite
P = proto-enstatite

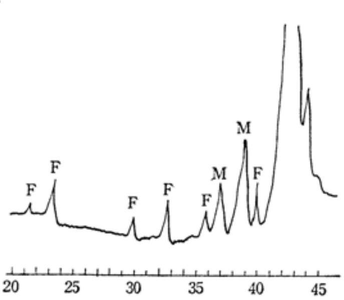

Fig. 14. X-Ray powder diffraction pattern of the surface of a MgO (singl.) piece reacted with a SiO_2(poly.) piece at 1500°C for 70 hr. (CuKα, 30 kV., 10 mA)
M = magnesia F = forsterite

---

[5] N. L. Bowen and O. Andersen, *Am. J. Sci.*, **37**, 488 (1914).

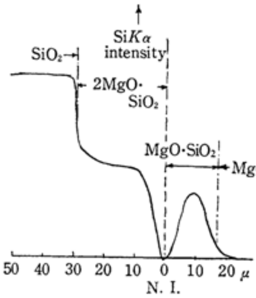

Fig. 15. Electron microprobe scanning figure as drawn perpendicular to the interface of a MgO-(singl.)-SiO_2(poly.) couple fired at 1500°C for 70 hr.
N.I.=new interface

E.P.M.A. conditions (Si$K\alpha$)

accerating voltage	25 kV.	absorption current	0.29 μA
analyzing crystal	mica	gain	16
scanning speed	10 μ/min		

Reaction in the MgO-TiO_2 (MgO Single Crystal - TiO_2 Single Crystal) System. In this system three compounds, $2MgO \cdot TiO_2$, $MgO \cdot TiO_2$ and $MgO \cdot 2TiO_2$, have been recognized.⁶⁾ After a reaction at 1400°C for 40 hr, the pair was easily separated into two pieces. On the reaction face of the MgO piece there existed no reacted substance, but there was a slight hollow at a contact part with the TiO_2 piece; only on the reaction face of the TiO_2 piece were there reacted products adhering closely to it. Figure 16 shows an X-ray powder diffraction pattern of the reaction face of the TiO_2 piece; it shows that $MgO \cdot TiO_2$ exists in a random orientation with a small amount of $2MgO \cdot TiO_2$. Figure 17, a scanning figure of the electron-probe microanalysis, shows that there is a low Mg-content layer in the inner part of the $MgO \cdot TiO_2$ layer. This layer seems to be $MgO \cdot 2TiO_2$, although it was not confirmed by X-ray diffraction analysis. From these results, the reacted layer may be supposed to be as Fig. 18.

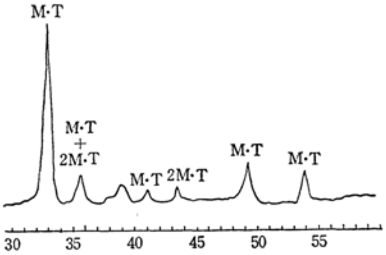

Fig. 16. X-Ray powder diffraction pattern of the surface of a TiO_2(singl.) piece reacted with a MgO(singl.) piece at 1400°C for 40 hr. (Cu$K\alpha$, 30 kV., 10 mA)
M·T=$MgO \cdot TiO_2$ 2M·T=$2MgO \cdot TiO_2$

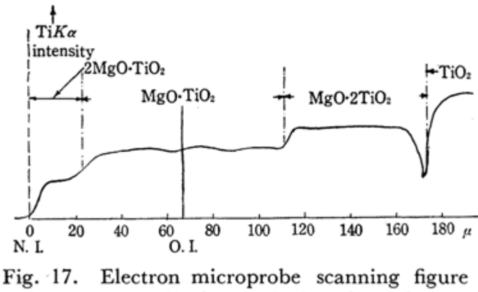

Fig. 17. Electron microprobe scanning figure as drawn perpendicular to the interface of a MgO·(singl.)-TiO_2(singl.) couple fired at 1400°C for 40 hr.
O.I.=original interface N.I.=new interface
E.P.M.A. conditions (Ti$K\alpha$) same as in Fig. 5.

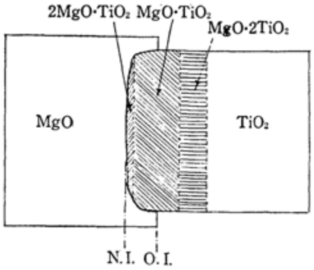

Fig. 18. Schematic section of a MgO(singl.)-TiO_2 (singl.) couple fired at 1400°C.
N.I.=new interface O.I.=original interface

Reaction in the CoO-TiO_2 (CoO Polycrystal-TiO_2 Single Crystal) System. In this system three compounds, $2CoO \cdot TiO_2$, $CoO \cdot TiO_2$, $CoO \cdot 2TiO_2$, have been recognized.⁷⁾ After a reaction at 1350°C for 70 hr, the pair was separated into two pieces. On the reaction face of the CoO piece there existed no reacted substance, but there was a slight hollow at a contact part with the TiO_2 piece, only on the reaction face of the TiO_2 piece were there reacted products adhering closely to the TiO_2 piece. Figure 19, an X-ray powder diffraction pattern of the reaction face of the TiO_2 piece, shows that only $2CoO \cdot TiO_2$ exists in a random orientation. Figure 20, a scanning figure of the

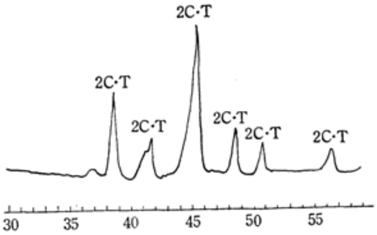

Fig. 19. X-Ray powder diffraction pattern of the surface of a TiO_2(sigl.) piece reacted with a CoO(poly.) piece at 1350°C for 70 hr. (Fe$K\alpha$, 28 kV., 8 mA)
2C·T=$2CoO \cdot TiO_2$

---

6) F. Massazza and E. Sirchia, *Chim. Ind.*, **40**, 378 (1958).

7) J. H. Strimple, Doctor Thesis, Rutgers University (1957).

electron-probe microanalysis, shows the Co contents change in three steps, corresponding to $2CoO{\cdot}TiO_2$, $CoO{\cdot}TiO_2$, and $CoO{\cdot}2TiO_2$ respectively. The confirmation of $CoO{\cdot}TiO_2$ and $CoO{\cdot}2TiO_2$ by X-ray diffraction, however, was difficult because of the thinness of the reacted layer. From these results the reacted layer may be supposed to be as is shown in Fig. 21.

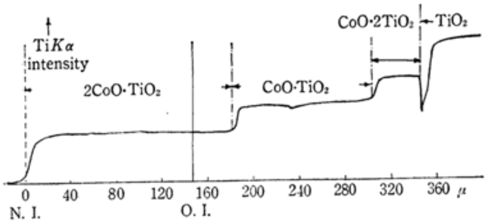

Fig. 20. Electron microprobe scanning figure as drawn perpendicular to the interface of a CoO-(poly.)-TiO_2(singl.) couple fired at 1350°C for 70 hr.
O.I. = original interface N.I. = new interface
E.P.M.A. conditions (Ti$K\alpha$) same as in Fig. 5.

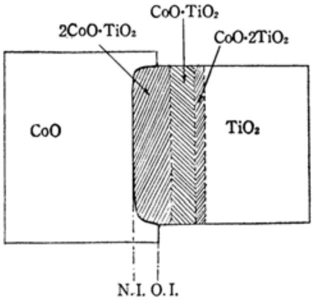

Fig. 21. Schematic section of a CoO(poly.)-TiO_2 (singl.) couple fired at 1350°C
N.I. = new interface O.I. = original interface

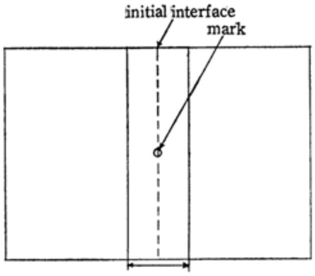

Fig. 22. Schematic section showing the place of a mark. The mark lies amidst the reacted substance showing counter diffusion.

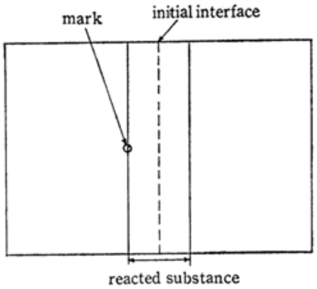

Fig. 23. Schematic section showing the place of a mark. The mark lies at the interface of the reacted substance and one of the reactants. This does not necessarily mean onesided diffusion.

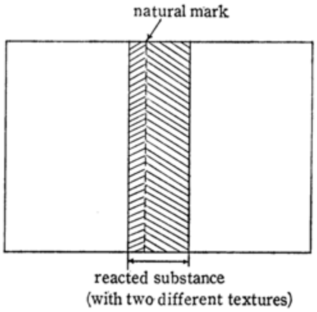

Fig. 24. Schematic section showing a natural mark.

Discussion

Determination of the Diffusion Form. It has been understood that the combining reaction between two oxides proceeds as a result of the diffusion of ions through the diffusion field of the reacted product. As typical forms of the diffusion the following three types have been proposed by many investigators; the counter diffusion of cation, the one-sided diffusion of one cation, accompanied by the parallel diffusion of the oxygen ion, and the one-sided diffusion of one cation, accompanied by the parallel transport of oxygen gas. To determine the diffusion form, the mark method and the texture analysis method are applied. The mark method is proper for determination of the cation counter diffusion if the product crystal growth takes place on both sides of the mark, as in Fig. 22, however, there is a danger of misunderstanding if a movement of the mark from the initial interface takes place, as in Fig. 23, because of the crystal growth which proceeds between the mark and the product pushing the mark. Therefore, even if the features of Fig. 23 occur, they can not be considered sure evidence of the one-sided diffusion through the diffusion field of the lattice. The texture-analyzing method is sometimes reliable for the determination of the cation counter diffusion if the textures formed on both sides of the initial interface can be discriminated, as in Fig. 24, but because the textures on both sides can not always be discriminated, a uniform texture can not be sure evidence of the one-sided diffusion. Thus it seems to be very difficult to prove the one-sided diffusion. As is shown in Fig. 25, sometimes in the powder reaction such a one-sided crystal formation as when a product crystal is formed, surrounded only by a definite substance, is observed;

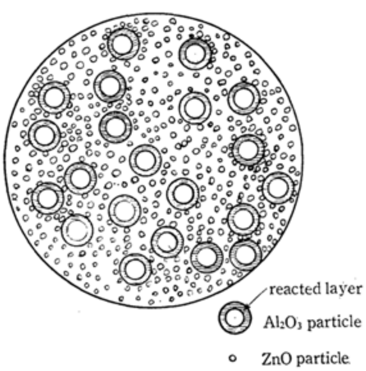

Fig. 25. Schematic figure of a powder reaction between ZnO and Al_2O_3.

this is apt to be considered as evidence for the one-sided diffusion.8) However, this phenomenon only shows which is a host crystal, it does not show a diffusion form through the diffusion field of the lattice, because this phenomenon can also take place in the case of the cation counter diffusion through the lattice. As far as the diffusion through the space is concerned, however, this phenomenon can be called the one-sided diffusion. Here the term "the diffusion through the space" means, for instance, the gas phase transport through the pore and crack, and the inter-contact-face transport (from one contact face to another), but not the diffusion through the diffusion field of the rigid lattice. As another type of the diffusion, that through the surface should also be considered.

MgO-Al_2O_3 and ZnO-Al_2O_3 Systems. In the present authors' experiment, Al_2O_3 became a host crystal, and, adhering closely to it, a spinel was formed. In respect to $MgO \cdot Al_2O_3$ the results are almost coincident with those of Rossi *et al.*9) Moreover, in respect to $ZnO \cdot Al_2O_3$, it is coincident with Hild's report8) that, in a reaction of the powder mixture, $ZnO \cdot Al_2O_3$ is formed only surrounding the Al_2O_3 grain. Carter10) and Rossi *et al.*9) maintained the cation counter diffusion through the formed spinel layer for the mechanism of $MgO \cdot Al_2O_3$ formation; the former studied the spinel formation, putting a mark at the initial interface, and found it at an inner part of the spinel layer, while the latter analyzed a formed spinel layer and found it to consist of two kinds of layers with different textures. Hild,8) following to the above-mentioned finding, and Bengston *et al.*11) and Branson,12) after their mark method experiment, maintained the one-sided diffusion of the Zn ion, accompanied by the parallel diffusion or the gas phase transport of oxygen, for the mechanism of $ZnO \cdot Al_2O_3$ formation. Lindner13) supported this mechanism from the standpoint of kinetics. On the other hand, Stone *et al.*14) and Pettit *et al.*15) maintained that all kinds of the $RO \cdot Al_2O_3$-type spinel formation take place, with a cation counter diffusion through the formed spinel layer, though without any experimental proof in the case of the $ZnO \cdot Al_2O_3$ formation. However the present authors have proved that also in the case of $ZnO \cdot Al_2O_3$ the reaction proceeds with the cation counter diffusion on the basis of the fact that the formed spinel had two kinds of textures. As we have said above, Hild's experiment is proper only for examining the adhering property, but improper for examining the diffusion form, and the mark method is also improper for obtaining evidence for the one-sided diffusion. Therefore, to make the spinel texture a natural mark is sometimes more reliable, as Pettit *et al.* have pointed out in their experiment on $NiO \cdot Al_2O_3$ formation. A growing ratio of two kinds of spinel textures in the case of the $MgO \cdot Al_2O_3$ formation has been found to be about 1 to 3 in Carter's experiment, and 1 to more than 3 in Rossi's8) and the present authors' experiments. The difference may be due to the differences in the experimental conditions, as Rossi has discussed.9) Carter measured the thickness of the spinel layers after equilibrium had been attained, while in Rossi's and the authors' experiments an effect of solid solution was taken account of. The ratio has been interpreted by Rossi.9) In the case of $ZnO \cdot Al_2O_3$ formation, the ratio was about 1 to 3 in the present authors' experiment. This ratio is reasonable, because the $ZnO \cdot Al_2O_3$ layer was found by electron microprobe analysis to have no distinguished concentration gradient.

MgO-Fe_2O_3 System. A feature of this system is that it forms a MgO-FeO-Fe_2O_3 solid solution, especially at high temperatures. Even at 1200°C this solid solution is formed, as is shown in Fig. 5 and Fig. 7. The rate of spinel formation seems to depend on the cation counter diffusion ($Mg^{2+} \rightleftharpoons Fe^{2+}, Fe^{3+}$) through the diffusion field of this solid solution as well as through that of the formed spinel layer. The MgO single crystal formed a solid solution in the single crystal state, while the polycrystalline MgO formed a polycrystalline solid solution. The rate of the counter diffusion in the single crystal was not as much as that in the polycrystalline state; therefore, the spinel formation shown in Fig. 6 is almost nothing, while that

---

8) K. Hild, *Z. Physik. Chem.*, **161**, 305 (1932).
9) R. C. Rossi and R. M. Fulrath, *J. Am. Ceram. Soc.*, **46**, 145 (1963).
10) R. E. Carter, *ibid.*, **44**, 116 (1961).
11) B. Bengston and R. Jagitsh, *Kemi. Minerali. Geol.*, **24**, 1 (1947).
12) D. L. Branson, *J. Am. Ceram. Soc.*, **48**, 591 (1965).
13) R. Lindner and A. Akerstrom, *Z. Physik. Chem.*, **16**, 162 (1965).
14) F. S. Stone and R. H. D. Tilley, "Reactivity of Solids," Elsevier Publishing Company, Amsterdam (1965), p. 583.
15) F. S. Pettit and E. H. Randkler, *J. Am. Ceram. Soc.*, **49**, 199 (1966).

shown in Fig. 4 is quite much. In the MgO-Fe_2O_3 system the spinel formation develops also from the R_2O_3 side to make it a host crystal, as is shown in Fig. 4. This result corresponds to Kuczynski's report[16] in which he mentioned that, in a reaction at 1300°C in air, Fe_2O_3 swelled into the MgO side, forming a MgO·Fe_2O_3 spinel and a solid solution ahead of the spinel. Carter[10] reported that, in the reaction between an MgO single crystal and a Fe_2O_3 polycrystal at 1370°C in an oxygen atmosphere, the ratio of the two kinds of spinel texture was 1 to 2.7, but in the authors' experiment such textures could not be discriminated. In the reaction at 1500°C, however, the reduction of Fe_2O_3 and the solid solution formation seemed to become more dominant than the spinel formation on the Fe_2O_3 side. Therefore, the original MgO piece seemed to swell and intrude into the Fe_2O_3, piece as is shown in Fig. 9. This reacted and swelled part in the MgO piece consists of both a MgO-type solid solution and a spinel, its Fe content was found by the electron probe microanalysis to be over 50 wt% of Fe_2O_3. From the phase diagram of the MgO-Fe_2O_3 system in air[3], it can be understood that about 50 wt% of Fe_2O_3 can enter the MgO lattice at 1500°C. Taking account of this fact, the spinel in the reacted and swelled part of the MgO piece seems to result both from the oversaturation of the solid solution during the reaction period and from segregation out of the solid solution during the cooling period.

MgO-Cr_2O_3 System. The authors' results were almost coincident with Schmalzried's.[17] A feature of this reaction is that the RO-type crystal (MgO) becomes a host crystal, unlike other spinel formations. The reasons for this may be that Cr_2O_3 is very volatile compared to MgO and that Cr_2O_3 can enter into the MgO lattice to form a solid solution. Thus volatile Cr_2O_3 will first enter into MgO to form a solid solution, its oversaturation may yield spinel which has a structure with the oxygen packing completely succeeding to that of MgO. The form of the diffusion through the formed spinel could not be determined.

MgO-SiO_2 System. Brindley *et al.*[18] reported, that in the reaction between polycrystalline MgO and SiO_2 specimens, 2MgO·SiO_2 was formed on the SiO_2 side by the one-sided diffusion of MgO into SiO_2; nevertheless, they referred to Shaw's report,[19] in which the formation of 2MgO·SiO_2 on the MgO side is discussed. In the authors' experiment, however, 2MgO·SiO_2 was formed adhering to the MgO side, while MgO·SiO_2 was formed adhering to the SiO_2 side. As to the form of diffusion, no definite conclusion could be drawn from these results.

MgO-TiO_2 System. Jander *et al.*[20] mentioned that, in the powder reaction between MgO and TiO_2, MgO·TiO_2 was formed at the first stage of the reaction from a mixture of any ratio; subsequently, MgO·TiO_2 was formed very easily from a mixture of the MgO-2TiO_2 ratio, while 2MgO·TiO_2 was formed very slowly from a mixture of the 2MgO-TiO_2 ratio. The authors' diffusion experiment can give a reason for these phenomena. The relatively wide MgO·2TiO_2 layer, compared to the 2MgO·2TiO_2 layer, seems to show that MgO·2TiO_2 is more easily formed than 2MgO·TiO_2. It is clear that a host crystal is TiO_2, but the form of diffusion is not clear from the reasons described above.

CoO-TiO_2 System. Schmalzried[20] reported that, in the reaction between polycrystalline pieces of CoO and TiO_2, 2CoO·TiO_2 was formed mainly, and that the diffusion form was the counter diffusion of cations in a nitrogen atmosphere, but a one-sided diffusion in an oxygen atmosphere. In the authors' experiment, however, three layers of different compounds were formed, all adhering to TiO_2, as is shown in Fig. 21; no evidence was obtained as to the diffusion form.

Conclusion

The existence of the counter diffusion as one of the diffusion forms through the field of the lattice has been established by the experiments of many investigators, but whether or not the one-sided diffusion exists as another diffusion form through the field is very difficult to determine, because no experiment which surely proves the one-sided diffusion through the lattice has ever been conducted. In order to solve this problem, unique experimental and analytical methods are necessary. However, with respect to the diffusion through the space, the one-sided diffusion can definitely take place; the mechanism of the crystal growth adhering selectively to a definite substance, as in the case of the powder reaction between ZnO and Al_2O_3, can be called in this meaning a "one-sided diffusion." Therefore, in the analysis of solid state reactions investigators must be careful to discriminate the diffusion through the diffusion field of the lattice from that through the space.

---

[16] G. C. Kuczynski, " Reactivity of Solids, Elsevier " Publishing Company, Amsterdam (1965), p. 352.

[17] H. Schmalzried, *Ber. Deut. Keram. Ges.*, **42**, 11 (1965).

[18] C. W. Brindley and Hayami, *Phil. Mag.*, **12**, 505 (1965).

[19] Shaw, Ph. D. Thesis, University of California (1956).

[20] W. Jander and K. Bunde, *Z. anorg. u. allgem. Chem.*, **239**, 418 (1938).

[21] H. Schmalzried, *Z. Physik. Chem.*, **33**, 111 (1962).