Role of Oxygen in Spinel Formation from MgO and Al₂O₃

By

Mitsuko NAKANO, Goro YAMAGUCHI and Kazuya SAITO

(Department of Industrial Chemistry, Faculty of Engineering, University of Tokyo, Tokyo)

1. Introduction

An understanding of the mechanism of solid state reaction remains imperfect because of the complexity of phenomena. Many investigations have been conducted on spinel formation from AO and B₂O₃ type oxides and the characteristics have been clarified little by little. However some investigations seem to have given misleading informations, and it is necessary to re-examine the spinel formation in order to obtain unambiguous knowledges. Especially on the role of oxygen, almost all investigations have been carried out by the marker method and the conflicting conclusions have often been drawn. Therefore the use of ¹⁸O, one of the stable isotopes of oxygen, as a tracer is considered to be useful for the study of the role of oxygen. If ¹⁸O is immobile, it serves as a marker, while if mobile, its concentration gradient may be detected.

Holt¹⁾ studied the formation of CoAl₂O₄ from CoO and Al₂O₃ using oxides enriched in ¹⁸O, and he concluded that CoO and Al₂O₃ react by the interdiffusion of Co and Al ions through a rigid oxygen lattice. In his study the oxygen mobility was followed by radioactivation of ¹⁸O by proton bombardment to yield the radioisotope, ¹⁸F, and the oxygen distribution in the product phase was indicated by autoradiography. This method, however, has some shortcomings. For instance some elements cause considerable background activity, and the extent of the application of this technique is limited.

The present authors²⁾ reported previously on the technique of analysis of ¹⁸O in solid oxides by spark source mass spectrometry. The application of this technique will give unambiguous informations about the mechanisms of solid state reactions in various oxides systems. In this investigation the MgO and Al₂O₃ system was selected to be examined by the spark source mass spectrometry technique, because the characteristics of the reaction in this system had been clarified in some detail.

2. Experimental

2.1 Preparation of specimens

(1) Polycrystalline MgO enriched in ¹⁸O.

Powder of ¹⁸O-enriched MgO was prepared from magnesium metal strips and ¹⁸O-enriched water by the following reactions:

carried out at 850°C for 6 hours,

carried out at 1,000°C in an argon atmosphere. Powder of ¹⁸O-enriched MgO was pressed into a tablet with about 2 cm diameter under the pressure of 2 ton/cm². Then the tablet was sintered well in an argon atmosphere at 1,550°C for 24 hours. A surface of the sintered specimen was polished with SiC grains and diamond paste.

(2) Single crystal of Al₂O₃. A single-crystalline boule of Al₂O₃ prepared by the Bernoulli method was cut perpendicularly to *c*-axis. Quarried *c*-plane was polished with SiC grains and diamond paste, and the specimen with a smooth surface was obtained.

(3) Polycrystalline Al₂O₃. Alumina powder prepared by calcining of gibbsite at 1,300°C was pressed into a tablet with about 2 cm diameter under the pressure of 2 ton/cm². The tablet was sintered well at 1,550°C for 24 hours. A surface of the sintered specimen was polished as well.

2.2 Spinel formation

Polished faces of the ¹⁸O-enriched MgO piece and the Al₂O₃ piece were placed so as to touch closely and they were heated in an argon atmosphere in a controlled electric furnace as shown in Fig. 1. The reactions were carried out at 1,615°C for 170 hours in case of Al₂O₃ single crystal and for 162 hours in case of Al₂O₃ polycrystal.

2.3 X-ray analysis and microscopic observation

After the reaction the MgO piece separated easily from the spinel adhering tightly to the Al₂O₃ piece. The spinel surface of contact with MgO was tested with an X-ray diffractometer in order to measure the lattice constant and determine the composition of the spinel. Then the spinel adhering to the Al₂O₃ piece was cut perpendicularly to the reaction face with a diamond cutter as shown

Fig. 1. Apparatus for the reaction in an argon atmosphere.

Fig. 2. Schematic illustration of the steps in the analyses and the surfaces used for them.

in Fig. 2. The cut surface was microscopically tested by reflecting light.

2.4 Determination of the ¹⁸O distribution in the spinel layer

Spark source mass spectrometry was used for analysis of ¹⁸O, and the details of the procedures were described previously²⁾. The initial surface of the spinel was analyzed by mass spectrometry and then the thin spinel layer was ground off with SiC grains by hand. The thickness of the ground layer was measured by use of a micrometer gauge with an accuracy within $\pm 1 \mu$. Then the new surface was analyzed as well to determine

Table 1. Experimental conditions for the mass spectrometry.

Analysis facility	JMS-01 B(M) double focussing, spark source mass spectrometer
Vacuum conditions	
Magnetic analyzer	$\sim 10^{-6}$ mmHg
Electrostatic analyzer	$\sim 10^{-6}$ mmHg
Ion source	$\sim 2 \times 10^{-7}$ mmHg while sparking
Instrument parameters	
Pulse duration	40 μ sec
Repetition rate	10 cycles/sec to 300 cycles/sec
Pulse power	4 kV
Accelerating voltage	20 kV
Electrostatic voltage	2.0 kV
Magnetic field	5.3 kG
Main slit	15 μ
Detector	50 $\times$ 380 mm Ilford Q2 photoplate

the ¹⁸O concentration at that position. The processes of grinding and measuring were repeated and the ¹⁸O distribution in the spinel layer was determined. Table 1 shows the experimental conditions for mass spectrometry. The ¹⁸O concentration in the ¹⁸O-enriched MgO piece was measured as well.

3. Results

3.1 X-ray analysis

As a result of X-ray analysis the composition of the spinel at the surface of contact with the MgO piece was recognized to be consistent with that of spinel in equilibrium with MgO. Then it was found that the adhesive condition of the reaction couple was good.

3.2 Microscopic observation

The spinel layer consisted of two layers with different textures. The total and respective thicknesses were measured as listed in Table 2.

Table 2. Results of microscopic test.

Texture of Al ₂ O ₃ piece	Reaction temp. (°C)	Reaction time (hr.)	Total thickness of spinel layer (μ)	Thickness of MgO-side layer (μ)	Thickness of Al ₂ O ₃ -side layer (μ)
Single crystal	1,615	170	960	170	790
Polycrystal	1,615	162	920	150	770

3.3 Mass spectrometry

The obtained ¹⁸O concentrations at the measured planes are listed in Table 3. The ¹⁸O concentration distributions are shown in Fig. 3 and Fig. 4, and the microscopic photographs of the spinel layers are displayed together.

4. Discussions

It is well known that the spinel layer formed by the reaction of MgO and Al₂O₃ consists of two layers; one is a thick layer continuous with the Al₂O₃ crystal and the other is a thinner layer grown on the outer side. Fig. 3 and Fig. 4 show that the ¹⁸O concentration changes very sharply at the interface of two spinel layers. It was

Table 3. The ^{18}O concentrations measured by spark source mass spectrometry.(A) The reaction couple of the ^{18}O -enriched MgO polycrystal and the Al_2O_3 single crystal.

Specimen	Distance from the MgO/spinel interface x (μ)	Concentration of ^{18}O , $\frac{^{18}\text{O}}{^{16}\text{O}+^{18}\text{O}}$ (atom %)
MgO piece		6.0
Spinel layer	0	6.2
	50	5.5
	70	5.4
	100	5.9
	140	6.1
	150	5.7
	160	2.7
	170	3.0
	180	0.24
	190	0.23
	300	0.23
	580	0.21
	730	0.17
	860	0.22
Al_2O_3 piece		0.23

(B) The reaction couple of the ^{18}O -enriched MgO polycrystal and the Al_2O_3 polycrystal.

Specimen	Distance from the MgO/spinel interface x (μ)	Concentration of ^{18}O , $\frac{^{18}\text{O}}{^{16}\text{O}+^{18}\text{O}}$ (atom %)
MgO piece		2.2
Spinel layer	0	2.0
	50	2.0
	100	2.2
	115	1.8
	130	1.4
	140	1.2
	155	0.28
	170	0.28
	450	0.28
	540	0.27
Al_2O_3 piece		0.24

concluded that the MgO-side spinel layer consists of oxygen which comes from the ^{18}O -enriched MgO piece and the Al_2O_3 -side spinel layer consists of oxygen from the Al_2O_3 piece.

The following mechanisms are suggested generally for spinel formation from AO and B_2O_3 type oxides: (1) Interdiffusion of two cations (2) parallel diffusion of A and oxygen ions (3) parallel diffusion of B and oxygen ions (4) diffusion of the A or B ions and electrons through the lattice accompanied by oxygen transport through the gas phase. If oxygen were one of the mobile ions and transported through the lattice, the ^{18}O concentration would decrease continuously from the MgO/spinel boundary all the way to the spinel/ Al_2O_3 boundary. If oxygen were transported through the gas phase, the Al_2O_3 -side spinel layer would contain ^{18}O considerably. The results displayed in Fig. 3 and Fig. 4 refute these assumptions and show that oxygen is immobile. The rate constant k calculated from the data listed in Table 2, $k=1.5 \times 10^{-8} \text{ cm}^2/\text{sec}$, is approximately equal to the estimated value about the reaction carried out in air at $1,615^\circ\text{C}$ on the basis of the data reported previously³⁾. Therefore it is sup-

Fig. 3. The microscopic photograph and the ^{18}O distribution in the spinel layer formed on the Al_2O_3 single crystal. The ^{18}O concentration rate is expressed in terms as follows:

$$\frac{(\text{observed concn.}) - (\text{natural abundance})}{(\text{conc. in the MgO piece}) - (\text{natural abundance})}$$

Fig. 4. The microscopic photograph and the ^{18}O distribution in the spinel layer formed on the Al_2O_3 polycrystal.

posed that the material transport in the spinel formation from MgO and Al_2O_3 in air is similar to that in an argon atmosphere. All informations obtained during this investigation support the

mechanism that Mg and Al ions diffuse in opposite directions with each other through a rigid oxygen framework.

During the spinel formation oxygen should migrate at the rate of the oxygen self-diffusion in spinel. It was difficult however to estimate the self-diffusion coefficient from the results obtained in this study, because the diffusion depth was very short and the sampling depth in the mass spectrometry was 5μ or thereabout in case of single crystal²⁾. The tentative value estimated from the ^{18}O distribution shown in Fig. 3 was $4 \times 10^{-13} \text{ cm}^2/\text{sec}$, and it is by far smaller than the diffusion coefficient of cations in spinel at $1,615^\circ\text{C}$, $\sim 1 \times 10^{-8} \text{ cm}^2/\text{sec}$.

In case of the spinel formed on Al_2O_3 polycrystalline piece the ^{18}O concentration seems to change at the position shifted slightly from the interface of two spinel layers as displayed in Fig. 4. Explanation is given as follows: The spinel formed on the sintered Al_2O_3 piece is polycrystalline, while that formed on the Al_2O_3 single crystal is rather single-crystalline. And the dimensions of craters produced on a polycrystalline specimen at the time of spark excitation are larger than those in case of single crystal. Therefore in case of single crystal the values of the ^{18}O concentration are measured from short ranges, on the contrary in case of polycrystal the values may be the mean concentrations measured from rather thick ranges, and the sampling depth was estimated to be about 15μ by the microscopy in the case shown in Fig. 4.

The mechanism of the spinel formation from MgO and Al_2O_3 has been an important research subject for several workers. Wagner⁴⁾ first suggested that such reaction occurs by interdiffusion of cations through the anion lattice of the product. Carter⁵⁾ carried out inert marker experiments in a hydrogen atmosphere and found that the marker lied within the spinel layer. Rossi *et al.*⁶⁾ analyzed a formed spinel layer and found that it consisted of two layers. Yamaguchi *et al.*⁷⁾ observed the same phenomenon. They all concluded that the Wagner mechanism describes the reaction between MgO and Al_2O_3 . Our present study have made clear the behaviours of oxygen during the spinel formation reaction, and reconfirmed the Wagner mechanism.

In respect to the spinel formation in other systems, almost all investigations reported previously were preformed by the inert marker method. In case of the reaction of ZnO and Al_2O_3 , Bengtson *et al.*⁸⁾ and Lindner *et al.*⁹⁾ concluded from their marker studies that zinc aluminate forms by zinc oxide diffusion through the product layer. On the other hand Yamaguchi *et al.*⁷⁾ maintained that the

reaction in the ZnO and Al_2O_3 system proceeds with the cation interdiffusion on the ground of the fact that the formed spinel had two kinds of textures. In case of nickel aluminate formation, Lindner *et al.*⁹⁾ concluded that the product forms by diffusion of Ni and oxygen ions through the aluminate. On the contrary, Pettit *et al.*¹⁰⁾ concluded from a natural marker study that the spinel layer forms by interdiffusion of Ni and Al ions. Such discrepancies between conclusions described above require a more detailed study. The technique used in this study will be applied effectively to re-examine the mechanism of the solid state reaction involving solid oxides.

5. Summary

The spinel layer formed through the reaction of the ^{18}O -enriched MgO piece and the Al_2O_3 piece in an argon atmosphere was analyzed by spark source mass spectrometry. It was found that the concentration of ^{18}O changes very sharply at the interface of two spinel layers. The ^{18}O distribution indicates that the MgO-side spinel layer consists of oxygen which comes from the ^{18}O -enriched MgO piece and the Al_2O_3 -side spinel layer consists oxygen from the Al_2O_3 piece. These results indicate the growing up of the spinel layers through the interdiffusion of Mg and Al ions in a rigid oxygen lattice of the product. The analysis method of ^{18}O in solid oxides by spark source mass spectrometry was demonstrated to be an effective technique for the investigation of solid state reactions. All solid state reactions about which incompatible observations were obtained should be re-examined by using ^{18}O as a tracer.

References

- 1) J.B. Holt, UCRL-12396 (1965).
- 2) M. Nakano, G. Yamaguchi and K. Saito, *Yogyo-Kyokai-Shi* **79** [2] 72-73 (1971).
- 3) G. Yamaguchi, K. Shirasuka and M. Munekata, *Yogyo-Kyokai-Shi* **79** [2] 64-69 (1971).
- 4) C. Wagner, *Z. physik. Chem. (B)* **34**, 309-16 (1936).
- 5) R.E. Carter, *J. Am. Ceram. Soc.* **44** [3] 116-20 (1961).
- 6) R.C. Rossi and R.M. Fulrath, *J. Am. Ceram. Soc.* **46** [3] 145-49 (1963).
- 7) G. Yamaguchi and T. Tokuda, *Bull. Chem. Soc. Japan* **40** [4] 843-51 (1967).
- 8) B. Bengtson and R. Jagitsch, *Arkiv Kemi, Mineral. Geol.* **24 A** [18] 1-16 (1947).
- 9) R. Lindner and Å. Åkerström, *Z. physik. Chem. [N.F.]* **6** [3/4] 162-77 (1956).
- 10) F.S. Pettit, E.H. Randklev and E.J. Felten, *J. Am. Ceram. Soc.* **49** [4] 199-203 (1966).

[Received July 7, 1970]

MgO-Al₂O₃ 系スピネル生成反応における酸素の役割

中野みつ子・山口 悟 郎・斎 藤 一 也

(東京大学工学部工業化学科)

MgO と Al₂O₃ よりスピネルが生成する反応について、酸素の役割をあきらかにする目的で、¹⁸O を過剰に含む MgO を用いて、研究を行った。¹⁸O を含む MgO の焼結体と、Al₂O₃ 単結晶または Al₂O₃ 焼結体とで反応カップルをつくり、アルゴン雰囲気中で、1,615°C で 170 時間または 162 時間、反応させた。Al₂O₃ 片に接着して生成したスピネル層について、スパーク放電形質量分析計を用いて分析し、スピネル層中の ¹⁸O の分布を

求めた。

その結果、MgO 側のスピネル層には、¹⁸O を含む MgO 試料と同じ濃度で ¹⁸O が分布し、Al₂O₃ 側のスピネル層には Al₂O₃ 試料と同じ濃度で ¹⁸O が分布していることが見出された。これより、MgO と Al₂O₃ からのスピネル生成反応は、スピネルの固定した酸素格子を通過しての Mg イオンと Al イオンの相互拡散によることが、明白に示された。