Study on the Reductive Spinel—A New Spinel Formula AlN-Al_2O_3 instead of the Previous One Al_3O_4

By Goro YAMAGUCHI and Hiroaki YANAGIDA

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It was proposed in the previous papers[1-3] that a lower valent aluminum ion Al^+ or Al^{2+} may exist in a spinel form Al_2O-$5Al_2O_3$ or Al_3O_4. L. M. Foster, however, suggested[4] that the spinel-like material contains nitride as its component and, therefore, the reducing ability is probably due to the nitride component.

In order to determine whether the reducing ability is due to the lower valent aluminum ion or to the nitride component, the chemical behaviors, the conditions of the formation, the magnetic susceptibility, the cell constant, and the density of the reductive spinel have been investigated.

Experimental

Synthesis of the Reductive Spinel.—Alumina and the reducing agent, aluminum or graphite, were mixed together and heated in the Tammann furnace (Fig. 1).

The X-ray diffraction patterns of the products were investigated at first, and the formation of the reductive spinel was confirmed with a number of methods as shown in Table I. The purity was confirmed also with the slow scanning X-ray diffraction recording.

Chemical Behaviors (Analysis of Nitrogen).—

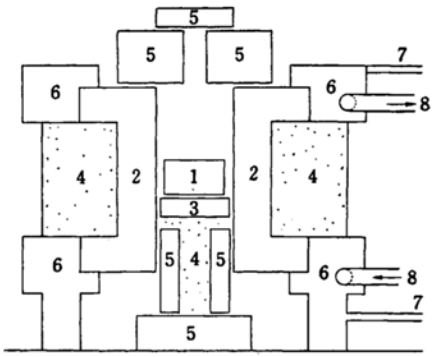

Fig. 1. Tammann furnace for the reductive spinel synthesis.
(1) sample, (2) graphite cylinder, resistance heater, (3) sintered alumina sample holder, (4) graphite powder, (5) refractory, (6) iron frame heater holder, (7) lead wire, (8) water, coolant.

The decomposition of the reductive spinel was tried by using the following reagents: (1) alkali or acid at room temperature; (2) PbO 90: B_2O_3 glass as a flux at 800°C in vacuo (Fig. 2); (3) air above 1000°C. The spinel employed in these experiments was confirmed not to show any X-ray diffraction pattern originating in crystalline aluminum nitride. The evolved gases in the

TABLE I. CONFIRMATION OF THE FORMATION OF THE REDUCTIVE SPINEL AND CHARACTERISTICS WHICH DISTINGUISH IT FROM OTHER SPINEL MgO-Al_2O_3 AND γ-Al_2O_3

	Methods	Reductive spinel	$MgO \cdot Al_2O_3$	γ-Al_2O_3
1)	X-ray diffraction recording (geigerflex, filtered Cu$K\alpha$ radiation) Scanning speed 4°2 θ per minute	Diffraction pattern of spinel structure Sharp peak	Diffraction pattern of spinel structure Sharp peak	Diffraction pattern of spinel structure Broad
2)	X-ray diffraction recording Scanning speed 1/4°2 θ per minute	Unit cell dimension about 7.94 Å	Unit cell dimension about 8.06 Å	Unit cell dimension about 7.89 Å
3)	Observation of Becke's line; comparison with the refractive index 1.74 of CH_2I_2	>1.74	<1.74	<1.74
4)	Observation of weight increase above 1000°C through heating in air	Increase	—	—

1) G. Yamaguchi, *J. Electrochem. Soc. Japan* (*Denki-Kagaku*), **14**, 106 (1946).
2) G. Yamaguchi, *J. Ceram. Assoc. Japan* (*Yogyo Kyokai Shi*), **61**, 549 (1953); *Ceram. Abstr.*, **33**, 87*e* (1954); *Chem. Abstr.*, **48**, 3652*b* (1954).
3) G. Yamaguchi, This Bulletin, **23**, 89 (1950).
4) Private communication from Dr. L. M. Foster (ALCOA).

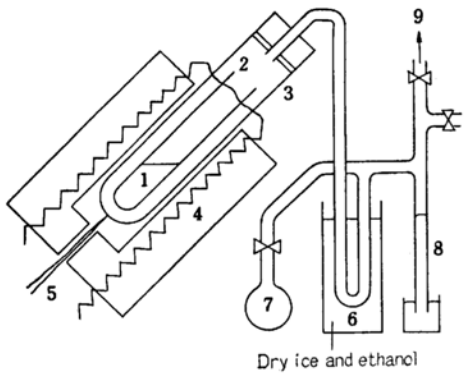

Fig. 2. Apparatus for nitrogen analysis.
(1) sample and flux, (2) silica tube, (3) transparent silica tube, (4) heater, (5) thermo-couple, (6) condenser, (7) gas sample flask, (8) pressure gauge, (9) vacuum pump.

decomposition process were analyzed by a mass-spectrometer.

Other Properties of the Spinel.—The magnetic susceptibility was measured by the Gouy method. The applied magnetic field was 8500 or 13000 gauss.

The mean dielelectric constant of the system of the spinel and air was measured. The frequency applied was 1 MC. The size of the spinel was 60~80 in Tyler mesh. Its packing ratios were from 0.48 to 0.53.

Results

Formation of the Reductive Spinel.—The reductive spinel can be formed through reduction of alumina in a reductive atmosphere above 1650°C, but in vacuo, alumina evaporates. The best procedure in the present study is as follows: (1) mixing 0.2 g. of graphite with 5 g. of γ-alumina thoroughly; (2) heating it at 1700°C for 2 hr. in the Tammann furnace through which only a little air can pass; (3) quenching it. When the reduction of alumina is insufficient α-alumina remains, whereas crystalline aluminum nitride is isolated when the reduction has proceeded too far.

Chemical Behaviors. — The decomposition of the reductive spinel by acid or alkali can not be noticed at room temperature. Products of the reaction between the reductive spinel and the glass as a flux were lead metal and nitrogen gas. The volume of the emitted nitrogen gas corresponds to 85% of the calculated value from the formula of $AlN-Al_2O_3$. The volume of nitrogen gas was fluctuated because of the difficulties of complete fusing. The emitted gas moved the flux to a lower temperature part. The sample increased in weight by 6.90% when it was kept in air above 1000°C, and turned into α-alumina.

Other Properties.—The observed magnetic susceptibility was $\chi = -0.34\times10^{-6}$/g. The dielectric constant was calculated to be 23.8. The refractive index 1.80 was also calculated from data[3]. Then, the ionic refraction of nitrogen N^{3-} in the reductive spinel should be 4.30. This calculation was made by the Lorentz-Lorenz equation. The unit cell dimension is 7.940 Å (in spinel structure *Fd3m*), and the density is 3.78 g./cc.

Discussion

The synthetic experiments show that the presence of nitrogen is inevitable in the conditions of the formation of the reductive spinel, and alumina turns into aluminum suboxide and evaporates in vacuo[5]. Emission of nitrogen gas and the weight increase of the reductive spinel through oxidation lead us to conclude that the reducing ability is due to the nitride component. The weight increase by 6.90% corresponds approximately to that of $AlN-Al_2O_3$ by 6.95%. The magnetic susceptibility shows an absence of lower valent aluminum ion Al^{2+}. The ionic refraction of nitrogen ion 4.30 in the spinel structure is only 1.14 times larger than that of oxygen ion 3.77[3]. This shows that the ionic radii of nitrogen ion is not much greater than that of oxygen ion. The density 3.78 g./cc. and the cell dimension 7.940Å are coincident with a spinel formula $AlN-Al_2O_3$.

Summary

A compound between aluminum oxide and aluminum nitride can be produced in a reductive atmosphere above 1650°C.

A new spinel formula $AlN-Al_2O_3$ should be adopted instead of the previous one $Al_2O-5Al_2O_3$ or Al_3O_4.

The physical constants of $AlN-Al_2O_3$ are as follows: crystal structure *Fd3m*, $Z=8$, $a=7.940$ Å; density 3.78 g./cc.; dielectric constant 23.8; refractive index 1.80; magnetic susceptibility -0.34×10^{-6}/g.

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

5) R. Kiyoura and T. Sata, *J. Ceram. Assoc. Japan (Yogyo Kyokai Shi)*, **66**, 44 (1958).