However, this can be minimized if the quantities of the rare earths adsorbed are sufficiently great that the length of the individual rare earth bands which develop are long compared to the diameter of the column. If the individual rare earth bands are short, a number of the binary mixtures obtained can be saved until a sufficient quantity has been accumulated to load another column.[6] One subsequent elution with EDTA will then separate a major portion of the two rare earths in a highly pure state.

These experiments do not establish optimum conditions for separation; however, they do demonstrate that rare earths can be separated rapidly by means of EDTA and that considerable quantities of pure rare earths can be obtained by this method in a period of four to five days with very little attention to the column operation being required during the interim period. We are continuing the study of these systems.

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[6] If one of the components of the binary mixture has a divalent state (Yb, Eu, Sm) a rapid chemical separation might be preferred at this point; see J. K. Marsh, H. N. McCoy.[7,8]

[7] J. K. Marsh, *J. Chem. Soc.*, 398, 523 (1942); 531 (1943).

[8] H. N. McCoy, This Journal, **58**, 2279 (1936); **63**, 1622 (1941).

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Formation, Stability and Crystal Structure of the Solid Aluminum Suboxides: Al_2O and AlO[1]

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The study of the reactions (1) $4Al(l) + Al_2O_3(s) \rightarrow 3Al_2O(s)$ and (2) $Al(l) + Al_2O_3(s) \rightarrow 3AlO(s)$ between 1000 and 2000°, by means of a high temperature X-ray technique, indicated the formation of solid Al_2O and AlO above certain temperatures. At 1000° no reaction occurs. Between 1100 and 1500° $Al_2O(s)$ is formed according to reaction 1. Between 1500 and 1600°, both reactions 1 and 2 occur simultaneously, whereas above 1600° the latter reaction occurs. On cooling or rapid quenching both compounds disproportionate into Al and Al_2O_3. From the X-ray diffraction patterns the crystal structure and lattice constants of Al_2O and AlO were determined. Both are cubic, the lattice constants being 4.98 Å. for Al_2O at 1110°, and 5.67 Å. for AlO at 1700°.

Introduction

The existence of gaseous AlO has been known from spectroscopic investigations.[2] From their investigation on the gaseous species of the $Al-Al_2O_3$ system, Brewer and Searcy[3] concluded that two suboxides of aluminum must exist in the gas phase; these they identified as Al_2O and AlO. A phase diagram study of $Al-Al_2O_3$, made by Baur and Brunner,[4] revealed the presence of a compound, Al_8O_9, melting at 2323°, with a eutectic between Al_8O_9 and Al_2O_3. Beletskii and Rapoport[5] reported the formation of hexagonal Al_2O by heating Al and Al_2O_3 *in vacuo* in the presence of SiO_2 and C and condensing the volatile products.

In the present investigation the formation, in the solid state, of the lower oxides of aluminum, which are not stable at room temperature, was studied by photographing X-ray diffraction patterns at high temperatures. The presence of a new compound is shown by the appearance of a new set of diffraction lines. By varying the temperature, the stability of the compound with respect to disproportionation into Al and Al_2O_3 can be determined. From the position of the lines in the diffraction patterns, lattice constants and crystal structure can be determined, and from the relative intensity of the pattern the approximate composition of the compound can be estimated.

Materials and Experimental Procedure

The X-ray diffraction patterns were taken in our high temperature camera which has been described elsewhere.[6] Besides the changes already made,[7] a new collimator was designed, which lowered the exposure time to 1 hour. This was necessary, due to the high evaporation rate of aluminum, even in the presence of 1 atm. of helium. The temperature was measured with a Leeds and Northrup disappearing-filament optical pyrometer which had been calibrated against a standard lamp obtained from the National Bureau of Standards. The temperature calibration of the camera was carried out by placing a "black body," made from a piece of tantalum tube, in place of the X-ray specimen. By taking account of the various calibration and correction factors, the uncertainty in the reading of the pyrometer, and the slight temperature variations during the runs, the temperature may be considered accurate to within 20°. Ni-filtered Cu $K\alpha$ radiation, obtained from a Machlett Tube operated at 50 kv. and 20 ma., was used.

The Al and Al_2O_3 were obtained from the J. T. Baker Chemical Co., and were of "Purified" and "Analyzed" grades, respectively. Rods of $^1/_{32}$ in. diameter and $^1/_4$ in. length were pressed from Al_2O_3 and Al_2O_3 + Al and placed into the camera. After filling with helium, the camera was heated and the X-ray diffraction patterns were photographed. For every X-ray determination a new sample was employed.

Experimental Results

The α-Al_2O_3 was found to have the same crystal structure at 2000° as at room temperature. Since aluminum is a liquid above 660°, it does not contribute any lines to the X-ray diffraction patterns.

Two sets, or series, of experiments were carried

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[1] This work was supported in part by the Office of Naval Research under contract with the Ohio State University Research Foundation.

[2] G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1950.

[3] L. Brewer and A. W. Searcy, This Journal, **73**, 5308 (1951).

[4] E. Baur and R. Brunner, *Z. Elektrochem.*, **40**, 155 (1934).

[5] M. S. Beletskii and M. B. Rapoport, *Doklady Akad. Nauk SSSR*, **80**, 751 (1951).

[6] J. W. Edwards, R. Speiser and H. L. Johnston, *Rev. Sci. Inst.*, **20**, 343 (1949).

[7] M. Hoch and H. L. Johnston, This Journal, **75**, 5224 (1953)

out: set no. 1 corresponded to the composition ratio 4:1 for Al:Al_2O_3, while set no. 2 corresponded to the ratio 1:1.

The X-ray diffraction patterns obtained from set no. 1 indicated that at 1000° no reaction occurred, while at 1100° a new set of lines (corresponding, as we will see later, to Al_2O), besides those for Al_2O_3, appeared. The diffraction pattern from Al_2O is consistent with a cubic structure having a lattice constant of 4.98 Å. The interplanar distances are given in Table I.

Table I

X-Ray Diffraction Lines of Al_2O at 1100°

Intensity	$\sin^2\theta$	d(in Å.)	Indices h,k,
Strong	0.0729	2.85	1,1,1
Medium	.1157	2.26	2,1,0
Medium	.2107	1.67	3,0,0 2,2,1
Weak	.3438	1.31	3,2,1

Diffraction patterns obtained from set no. 2 (Al:Al_2O_3 = 1:1) show that the Al lines, at room temperature, are much weaker than those from set no. 1. This is to be expected since the ratio of Al to Al_2O_3 is now 1:1 instead of 4:1. At 1100° the same new lines (those for Al_2O) appear as before, but they are much weaker. At 1500° another set of lines, belonging, as we will see later, to AlO, appear together with the Al_2O lines. At 1700° only the AlO lines appear. The AlO diffraction pattern leads to a cubic structure with a lattice constant of 5.67 Å. Interplanar distances are given in Table II.

Table II

X-Ray Diffraction Lines of AlO at 1700°

Intensity	$\sin^2\theta$	d (in Å.)	Indices h,k,l
Strong	0.0548	3.28	1,1,1
Medium	.0923	2.52	2,1,0
Medium	.1091	2.33	2,1,1
Weak	.1502	1.98	2,2,0
Medium	.2012	1.71	3,1,1

At 1900° the whole sample (15 mg.) vaporized within one hour, indicating that AlO has a high vapor pressure at that temperature.

On every pattern Al_2O_3 lines are present. This can be expected to be due to the fact that some Al evaporates during the exposures, thereby shifting the equilibria in the two reactions $4Al + Al_2O_3 \rightleftarrows 3Al_2O$ and $Al + Al_2O_3 \rightleftarrows 3AlO$ to the left. Because of the rapid disproportionation into Al and Al_2O_3, every attempt to obtain diffraction patterns for the two compounds at room temperature by rapidly quenching the samples was unsuccessful.

Discussion of Results

The investigation showed the existence of two lower aluminum oxides in the solid phase, each having a cubic structure, the lattice constants being 4.98 and 5.67 Å. The problem now is to decide which is Al_2O and which is AlO. Let us call the compound formed at 1100° "compound 1" and the one at 1700°, "compound 2."

All diffraction pictures were obtained using the same X-ray intensity and exposure time. The Al_2O_3 pattern is present on every picture with about the same intensity. Thus the relative intensity of the new diffraction patterns gives information as to how much Al is needed (compared to Al_2O_3) in the formation of the compounds. The ratio Al:Al_2O_3 was 4:1 in the first set, and 1:1 in the second set. A visual comparison of the intensities of the different diffraction patterns shows that the intensity of the new diffraction pattern in set no. 2 at 1700° is much stronger than that for the new diffraction pattern in this same set at 1100°, and that the intensity of the new pattern in this set at 1700° is about equal to that in set no. 1 at 1100°. For the same amount of Al, less of compound 1 is formed than of compound 2. Similarly, to form the same amount of material, more Al is needed for compound 1 than for compound 2. It therefore follows that compound 1 (at 1100°) is richer in Al than is compound 2. Thus compound 1 is Al_2O while compound 2 is AlO, as was assumed during the description of the patterns.

From the diffraction patterns obtained, the stability against disproportionation into Al and Al_2O_3 of the lower oxides in solid form can be deduced. Below 1000° only liquid Al and Al_2O_3 are stable. Al_2O is stable between 1050 and 1600° and AlO is stable above 1500°.

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