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Reaction between Aluminium Trichloride and Steam in the Vapor Phase and Properties of the Aluminium Oxide Formed

Yuichi Shoji, Ryoko Matsuzaki, and Yuzo Saeki*
Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259, Nagatsuta-cho, Midori-ku, Yokohama 227

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The reaction between gaseous $AlCl_3$ and steam, and the products formed were examined by X-ray analysis, TG, DTA, and electron microscopy. The thermal transitions of the Al_2O_3 formed under various conditions were also examined. The reaction between gaseous $AlCl_3$ and steam occurs even at 150 °C and proceeds rapidly above about 400 °C. The product is amorphous Al_2O_3 below 600 °C, amorphous Al_2O_3 containing poorly crystallized γ-Al_2O_3 at 800 °C, γ-Al_2O_3 containing amorphous Al_2O_3 at 900 °C, and γ-Al_2O_3 at 1000 °C. Also, it was observed that the Al_2O_3 formed below 900 °C included a chloride oxide of aluminium, which decomposed in the vicinity of 830 °C to form γ-Al_2O_3 with the evolution of gaseous $AlCl_3$. On heating the amorphous Al_2O_3 formed by the reaction between gaseous $AlCl_3$ and steam, the transition: amorphous $\xrightarrow{ca.\ 700\,^{\circ}\mathrm{C}} \chi \xrightarrow{ca.\ 800\,^{\circ}\mathrm{C}} \kappa \xrightarrow{ca.\ 1000\,^{\circ}\mathrm{C}} \alpha$ occurs; and on heating the γ-Al_2O_3 formed by the same reaction, the transition: $\gamma \xrightarrow{ca.\ 900\,^{\circ}\mathrm{C}} \delta \xrightarrow{ca.\ 1000\,^{\circ}\mathrm{C}} \theta \xrightarrow{ca.\ 1000\,^{\circ}\mathrm{C}} \alpha$ occurs.

The reaction of volatile metal chlorides with oxygen or steam has recently become important for the preparation of fine powders of pure metal oxides, because it is possible to carry out the reaction in the vapor phase. To develop a chemical process for preparing fine powders of aluminium oxide (Al_2O_3) by the vapor-phase oxidation of aluminium trichloride ($AlCl_3$), the authors1) have examined the reaction between $AlCl_3$ and oxygen in the vapor phase and the properties of the Al_2O_3 formed.

There are limited data on the reaction between $AlCl_3$ and steam in the vapor phase. Kato *et al.*2) have studied the reaction product between gaseous $AlCl_3$ and excess steam at 700—1100 °C and reported that the reaction product is amorphous Al_2O_3 which includes a Cl-containing compound, presumably AlClO, at 700 and 900 °C and δ-Al_2O_3 with or without a small amount of κ-Al_2O_3 at 1100 °C. They have also reported that the amorphous Al_2O_3 crystallizes to κ-Al_2O_3 on heating up to 830 °C in the air and that the δ-Al_2O_3 transforms to α-Al_2O_3 by the heat treatment at 1100 °C in the air.

In this paper, the reaction between gaseous $AlCl_3$ and steam and the product formed have been examined in detail by X-ray analysis, thermogravimetry (TG), differential thermal analysis (DTA), and electron microscopy. The thermal transition of the Al_2O_3 formed under various conditions has also been examined.

Experimental

The $AlCl_3$ used was prepared by the reaction between pure aluminium(Al:99.99%) and chlorine at 400 °C.1)

A transparent quartz reaction tube (1000 mm length) with an inner concentric tube was used. Gaseous $AlCl_3$ was formed by heating $AlCl_3$ placed in the inner tube at 150 °C, and was carried by a stream of argon (40 cm^3/min) to the reaction zone (27 mm i.d. and 250 mm length) held at a specified temperature. In the meantime, a stream of argon (100 cm^3/min) containing a specified amount of steam was introduced through a separate tube into the reaction zone. The mean flow-rate of the $AlCl_3$ was approximately 3.8 cm^3 Al_2Cl_6(g)/min. The reaction was allowed to proceed for 2 h.

Hydrogen chloride(HCl) formed during the reaction was absorbed in a known amount of 0.1 M[†] sodium hydroxide (NaOH) solution, and was determined by neutralization titration of the excess NaOH.

The unreacted $AlCl_3$, which was deposited outside the reaction zone together with the reaction product, was separated by heating the mixture in an argon stream at 250 °C. The $AlCl_3$ adsorbed on Al_2O_3 formed was separated by washing the Al_2O_3 with ethanol at boiling point with stirring.1)

X-Ray analysis of soild product was performed with an X-ray powder diffractometer equipped with a proportional counter, using Ni filtered Cu radiation. TG and DTA were performed in an argon stream and a heating rate of 5 °C/min was employed. The sensitivity of the quartz helix used for TG was approximately 71 mm/g. α-Al_2O_3 was used as a reference for DTA.

Throughout this work, $AlCl_3$ and reaction products were handled in an argon atmosphere or *in vacuo* to prevent any contamination from moisture in the air.

Results and Discussion

Reaction between Gaseous Aluminium Trichloride and Steam. The amounts of HCl formed by the reaction between gaseous $AlCl_3$ and steam(H_2O) at various temperatures were examined. When gaseous $AlCl_3$ and a stream of argon containing excess H_2O (15 vol% H_2O), more than the value calculated as needed to form Al_2O_3 and HCl, was introduced into the reaction zone, a part of the HCl formed by the reaction was dissolved in the unreacted H_2O which condensed outside the heating zone. Aluminium trichloride hexahydrate was also formed from the Al_2O_3 and the HCl. So, the experiments were thus carried out by introducing into the reaction zone a stream of argon containing an amount of H_2O (9, 5, or 2 vol% H_2O) smaller than the calculated value. The reaction temperature above 150 °C was employed, because gaseous $AlCl_3$ was generated by heating $AlCl_3$ at 150 °C. The results are shown in Fig. 1. The broken lines in Fig. 1 show the calculated values of the amount

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[†] 1 M=1 mol dm^{-3}.

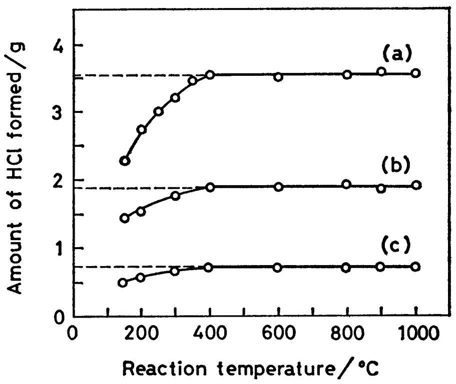


Fig. 1. Amounts of HCl formed by the reaction between gaseous $AlCl_3$ and steam at various temperatures.
Steam content in Ar: (a) 9 vol%, (b) 5 vol%, (c) 2 vol%.

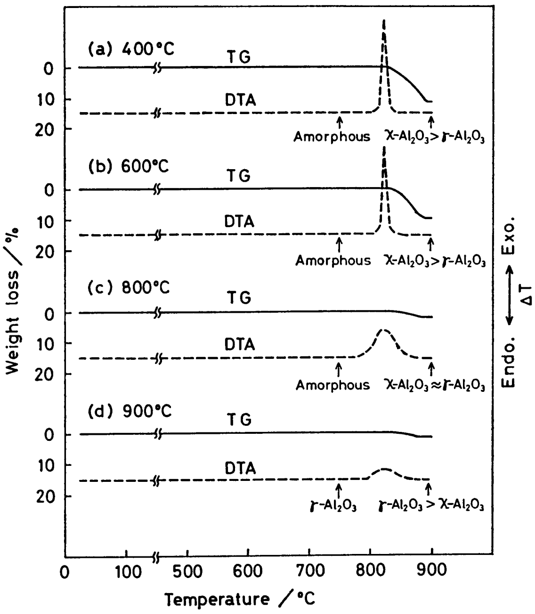


Fig. 2. TG and DTA curves of the products formed by the reaction between gaseous $AlCl_3$ and steam at 400—900 °C.

of HCl, based on the assumption that all the H_2O introduced reacts with gaseous $AlCl_3$ to form HCl. From the results, the reaction between gaseous $AlCl_3$ and H_2O begins even at 150 °C, and all the H_2O introduced reacts with gaseous $AlCl_3$ above about 400 °C.

To determine the reaction product of gaseous $AlCl_3$ with H_2O, the products formed by introducing a stream of argon containing 9 vol% H_2O at reaction temperatures above 400 °C were examined by X-ray analysis, TG, and DTA.

The X-ray analysis of the reaction products formed at 400 and 600 °C showed no diffraction line. The TG and DTA curves of the products are shown in Figs. 2(a) and (b).

The samples obtained after heating both the products up to 750 °C gave no change in X-ray diffraction pattern (amorphous). The samples obtained after heating up to 900 °C gave diffraction lines corresponding to both χ-Al_2O_3[3,4] and γ-Al_2O_3.[3,5] From these results and the fact that the amorphous Al_2O_3 formed by the reaction between gaseous $AlCl_3$ and oxygen crystallizes to χ-Al_2O_3 in the vicinity of 820 °C with an exothermic effect as previously reported,[1] the exothermic effect observed in the vicinity of 820 °C was considered to be due to the crystallization of amorphous Al_2O_3. During the weight losses in the vicinity of 830 °C which appeared in the TG curves (12% for the product at 400 °C; 10% for the product at 600 °C), it was observed that a white powder was deposited on a cooler part outside the heating zone. The white powder was identified as $AlCl_3$ by chemical analysis. This result and the fact that diffraction lines corresponding to γ-Al_2O_3 in addition to χ-Al_2O_3 based on the crystallization of amorphous Al_2O_3 were observed in both samples obtained after heating up to 900 °C led us to conclude that the products formed by the reaction at 400 and 600 °C were amorphous Al_2O_3 containing a compound which decomposed in the vicinity of 830 °C to form γ-Al_2O_3 with the evolution of gaseous $AlCl_3$. Also, the results of IR spectroscopy confirmed that the reaction products contained neither H_2O nor OH^-. These results indicated that the compound mentioned above was a chloride oxide of aluminium.

The reaction product formed at 800 °C was found to be amorphous by X-ray analysis and its TG and DTA curves are shown in Fig. 2(c). The exothermic effect due to the crystallization of amorphous Al_2O_3 in the vicinity of 820 °C became weak and diffuse. Although the weight loss in the vicinity of 830 °C (3%) was rather small compared with those of the reaction products formed at 400 and 600 °C, the sample obtained after heating up to 900 °C gave diffraction lines corresponding to both χ-Al_2O_3 and γ-Al_2O_3. These results indicated that the reaction product formed at 800 °C was amorphous Al_2O_3 containing poorly crystallized γ-Al_2O_3 and a small amount of the chloride oxide. This estimation was confirmed by the experimental results on the thermal transitions of the Al_2O_3 formed under various conditions, as described later.

The reaction product formed at 900 °C gave diffraction lines corresponding to γ-Al_2O_3. But the DTA curve (Fig. 2(d)) showed a weak exothermic effect due to the crystallization of amorphous Al_2O_3, and the sample obtained after heating up to 900 °C showed diffraction lines corresponding to χ-Al_2O_3 in addition to γ-Al_2O_3. Also, a slight weight loss (1%) due to the thermal decomposition of the chloride oxide was observed. These results indicated that the reaction product formed at 900 °C was γ-Al_2O_3 containing amorphous Al_2O_3 and a small amount of the chloride oxide.

The reaction product formed at 1000 °C gave diffraction lines corresponding to γ-Al_2O_3, and gave no thermal effect in the DTA, and no weight change in the TG. The sample obtained after heating up to 900 °C gave diffraction lines corresponding to γ-Al_2O_3 alone. From these results, the reaction product formed at 1000 °C was found to be γ-Al_2O_3.

The reaction products formed by introducing gaseous

TABLE 1. THERMAL TRANSITIONS OF Al_2O_3 FORMED AT VARIOUS TEMPERATURES

Heating temp °C	Formation temperature of Al_2O_3 and heating atmosphere							
	400 °C		600 °C		800 °C		900 °C	1000 °C
	In argon	In air	In argon	In air	In argon	In air	In argon and air	In argon and air
600	Amorphous		Amorphous		Amorphous		γ	γ
700	χ	χ	χ	χ	χ	χ	$\gamma>\chi$	γ
800	χ, κ, γ	χ, κ	χ, κ, γ	χ, κ	χ, κ, γ	χ, κ, γ	$\gamma>\chi$	γ
900	χ, κ, γ	χ, κ	χ, κ, γ	χ, κ	χ, κ, γ	$\chi, \kappa, \gamma \gg \delta$	$\gamma>\delta, \kappa$	γ, δ
1000	$\kappa, \delta>\alpha$	κ, α	$\kappa, \delta>\alpha$	κ, α	$\kappa, \delta, \theta, \alpha$	$\kappa, \delta, \theta, \alpha$	δ, θ, α	δ, θ, α
1100	α	α	α	α	α	α	$\alpha>\theta, \delta$	$\alpha>\theta, \delta$
1200	—	—	—	—	—	—	α	$\alpha>\theta$
1300	—	—	—	—	—	—	—	α

Amorphous: amorphous Al_2O_3, χ: χ-Al_2O_3, κ: κ-Al_2O_3,[3,6] γ: γ-Al_2O_3, δ: δ-Al_2O_3,[3,7] α: α-Al_2O_3,[8] θ: θ-Al_2O_3.[9]

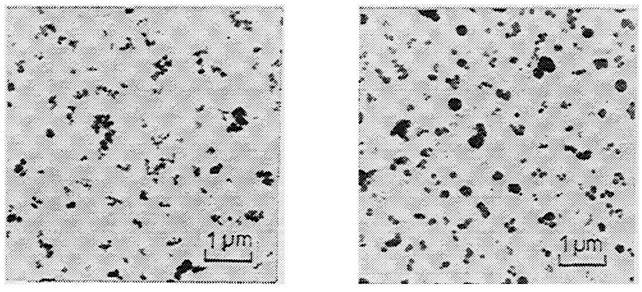
$AlCl_3$ and a stream of argon containing 5 vol% H_2O were examined in the manner described above. The results indicated that the reaction product at each temperature was similar to that formed by introducing a stream of argon containing 9 vol% H_2O, described above.

These experimental results show that the reaction between gaseous $AlCl_3$ and H_2O occurs even at 150 °C and proceeds rapidly above about 400 °C. The reaction product formed is amorphous Al_2O_3 at 400—600 °C, amorphous Al_2O_3 containing poorly crystallized γ-Al_2O_3 at 800 °C, γ-Al_2O_3 containing amorphous Al_2O_3 at 900 °C, and γ-Al_2O_3 at 1000 °C. In addition, the Al_2O_3 formed below 900 °C includes the chloride oxide of aluminium, which decomposes in the vicinity of 830 °C to form γ-Al_2O_3 with the evolution of gaseous $AlCl_3$. The amount of the chloride oxide decreased with increasing the reaction temperature, and the formation of the chloride oxide was not observed at 1000 °C.

Kato *et al.*[2] have reported that the products formed by the reaction between gaseous $AlCl_3$ and H_2O at 700 and 900 °C are amorphous and have estimated that the products include a Cl-containing compound, presumably AlClO, from the result that, on heating the products in the air, they lose weight in the vicinity of 800 °C with the evolution of chlorine. In the present work, it was also observed that the Al_2O_3 formed below 900 °C included a chloride oxide of aluminium. The only known chloride oxide of aluminium is AlClO. But, the composition of the chloride oxide formed in these experiments was not evaluated by chemical analysis, because the chloride oxide was included in the Al_2O_3 formed.

As described in the previous report,[1] the reaction between gaseous $AlCl_3$ and oxygen occurs above about 400 °C and proceeds appreciably above about 800 °C. While, the reaction with H_2O was found to proceed rapidly at rather low temperatures. The modification of the Al_2O_3 formed by the reaction with H_2O at each temperature was the same as that of the Al_2O_3 formed by the reaction with oxygen,[1] except that the Al_2O_3 formed by the reaction with oxygen at 800 °C is amorphous Al_2O_3.

The reaction products formed by introducing gaseous $AlCl_3$ and a stream of argon containing 9 or 5 vol% H_2O at various temperatures were examined by electron microscopy. Typical electron micrographs of the Al_2O_3 formed are shown in Fig. 3.



(a) 800°C (b) 1000°C

Fig. 3. Electron micrographs of the Al_2O_3 formed by the reaction between gaseous $AlCl_3$ and steam at 800 and 1000 °C (Steam content in Ar: 9 vol%).

As reported before,[1] the Al_2O_3 formed by the reaction with oxygen is relatively uniform, ultrafine powders with diameters of the order of 1/100 µm. While, the range of particle sizes of the Al_2O_3 formed by the reaction with H_2O was found to be wide, as seen from Fig. 3.

Thermal Transition of the Aluminium Oxide Formed by the Reaction between Gaseous Aluminium Trichloride and Steam. The thermal transitions of the Al_2O_3 formed under various conditions were examined. The samples obtained by heating the Al_2O_3 at a specified temperature for 2 h both in an argon atmosphere and in the air were examined by X-ray analysis.

The results for the Al_2O_3 formed by introducing a stream of argon containing 9 vol% H_2O are shown in Table 1. As examples, the X-ray diffraction patterns of the samples obtained after heating the amorphous Al_2O_3, formed at 400 °C, at various temperatures in an argon atmosphere and after heating the γ-Al_2O_3, formed at 1000 °C, at various temperatures in the air are illustrated in Figs. 4 and 5, respectively.

These experimental results show that, on heating the amorphous Al_2O_3, formed at 400 and 600 °C, both in an argon atmosphere and in the air, the amorphous $\xrightarrow{ca.\ 700\ °C} \chi \xrightarrow{ca.\ 800\ °C} \kappa \xrightarrow{ca.\ 1000\ °C} \alpha$ transition occurs regardless of the heating atmosphere. The γ-Al_2O_3 observed in the samples obtained after heating

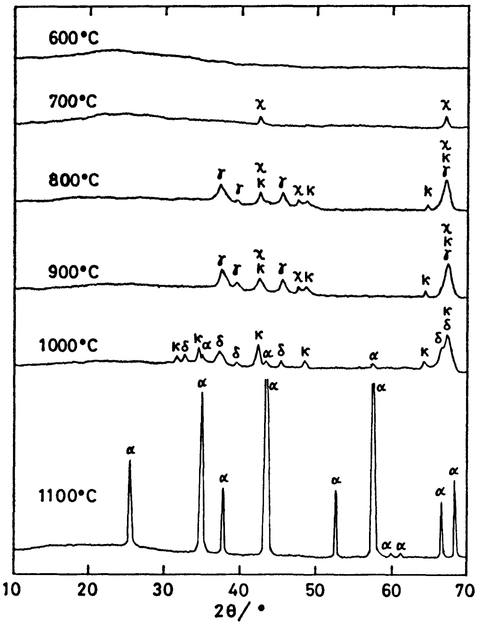


Fig. 4. X-Ray diffraction patterns of the samples obtained after heating the amorphous Al_2O_3, formed at 400 °C, at various temperatures in an argon atmosphere.

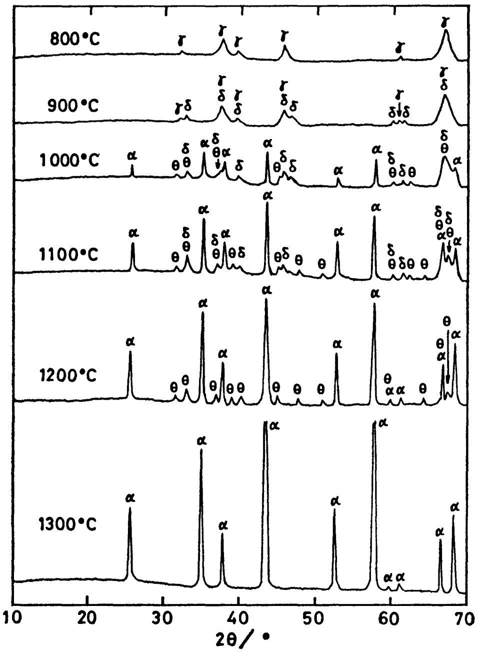


Fig. 5. X-Ray diffraction patterns of the samples obtained after heating the γ-Al_2O_3, formed at 1000 °C, at various temperatures in the air.

at 800 and 900 °C in an argon atmosphere was considered to be due to the decomposition of the chloride oxide, as mentioned before, and the δ-Al_2O_3 observed at 1000 °C was considered to be due to the thermal transition of the γ-Al_2O_3 formed. The samples obtained after heating the amorphous Al_2O_3 in the air gave neither diffraction lines corresponding to γ-Al_2O_3 nor diffraction lines corresponding to δ-Al_2O_3. This fact was considered to indicate that, on heating the chloride oxide in the air, it was oxidized to amorphous Al_2O_3, which transformed in the same manner as the amorphous Al_2O_3 formed by the reaction between gaseous $AlCl_3$ and H_2O.

The result for the γ-Al_2O_3 formed at 1000 °C indicates that, on heating the γ-Al_2O_3, the $\gamma \xrightarrow{ca.\ 900\ °C} \delta \xrightarrow{ca.\ 1000\ °C} \theta \xrightarrow{ca.\ 1000\ °C} \alpha$ transition occurs regardless of the heating atmosphere.

On heating the γ-Al_2O_3 containing amorphous Al_2O_3, formed at 900 °C, and the amorphous Al_2O_3 containing poorly crystallized γ-Al_2O_3, formed at 800 °C, both the amorphous$\rightarrow\chi\rightarrow\kappa\rightarrow\alpha$ and $\gamma\rightarrow\delta\rightarrow\theta\rightarrow\alpha$ transitions occur, as is expected from the above results.

As mentioned above, it was observed that, on heating the Al_2O_3 formed at 800 °C in the air, the $\gamma\rightarrow\delta\rightarrow\theta\rightarrow\alpha$ transition occurred. Also, let us assume that the γ-Al_2O_3 observed in the samples obtained after heating the Al_2O_3 formed at 800 °C both in an argon atmosphere and in the air is due to the thermal decomposition of the chloride oxide included in the Al_2O_3. Then θ-Al_2O_3 should not be observed in the samples obtained after heating at 1000 °C, as seen from the results obtained on heating the amorphous Al_2O_3, formed at 400 and 600 °C, in an argon atmosphere. These results support the estimation, described in the previous paragraph, that the Al_2O_3 formed at 800 °C is amorphous Al_2O_3 containing poorly crystallized γ-Al_2O_3.

The experimental results for the Al_2O_3 formed by introducing a stream of argon containing 5 vol% H_2O were similar to those for the Al_2O_3 formed at 9 vol% H_2O, described above.

These experimental results show that, on heating the amorphous Al_2O_3 formed by the reaction between gaseous $AlCl_3$ and H_2O, the amorphous $\xrightarrow{ca.\ 700\ °C} \chi \xrightarrow{ca.\ 800\ °C} \kappa \xrightarrow{ca.\ 1000\ °C} \alpha$ transition occurs, and on heating the γ-Al_2O_3 formed, the $\gamma \xrightarrow{ca.\ 900\ °C} \delta \xrightarrow{ca.\ 1000\ °C} \theta \xrightarrow{ca.\ 1000\ °C} \alpha$ transition occurs.

As previously reported,[1] on heating the amorphous Al_2O_3 formed by the reaction with oxygen, the amorphous $\xrightarrow{ca.\ 700\ °C} \chi \xrightarrow{ca.\ 800\ °C} \kappa \xrightarrow{ca.\ 1000\ °C} \alpha$ transition occurs. On heating the γ-Al_2O_3 formed, the $\gamma \xrightarrow{ca.\ 1000\ °C} \delta \xrightarrow{ca.\ 1100\ °C} \theta \xrightarrow{ca.\ 1100\ °C} \alpha$ transition occurs. The transition temperatures of $\gamma\rightarrow\delta$, $\delta\rightarrow\theta$, and $\theta\rightarrow\alpha$ on heating the γ-Al_2O_3 formed by the reaction with H_2O are approximately 100 °C lower than those of the γ-Al_2O_3 formed by the reaction with oxygen.

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