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Preparation of Aluminum Fluoride Film with Graphite Fluoride

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An aluminum fluoride film covered by graphite fluoride on metallic aluminum was prepared by reaction in the ternary system of aluminum, graphite and fluorine gas at 450—550 °C. The film consisted of a large amount of aluminum fluoride covered by thin graphite fluoride layers. The contact angle of a water drop on the film was around 120 °, which decreased to 85—95 ° during 45 d probably due to reaction with moisture and/or water drop. Almost no oxygen was detected in the film. The film formation would be based on the reduction of oxide layer on aluminum by carbon radical produced by thermal decomposition of graphite fluoride.

An aluminum fluoride film covered by graphite fluoride is formed by the reaction of metallic aluminum with graphite fluoride in a fluorine atmosphere at 450—600 °C.[1)]

$$Al + (CF)_n + F_2 \xrightarrow{450-600^\circ C} \text{Aluminum fluoride film with graphite fluoride} \quad (1)$$

This film had a low surface energy with a contact angle for a water drop, *ca.* 120 ° and was an electric insulator. The value of the contact angle is the same as that on the basal plane of graphite fluoride.[2)] The fluoride film is also prepared through another route of the ternary system of aluminum, graphite and fluorine gas,[1)] in which graphite fluoride would be preferentially formed and then react with aluminum.

In this study, the preparation and structure of the aluminum fluoride film with graphite fluoride was investigated in the ternary system of aluminum, natural graphite and fluorine gas.

Experimental

An aluminum plate (18×14×0.8 mm, purity: 99.99%) was used after immersion in 10% NaOH solution for 5 min and in 3 M† HNO_3 for 10 s to remove oily material on the surface. Other starting materials were Madagascar natural graphite (40—47 μm, purity: 99.4%) and high purity fluorine gas (99.4%).

The fluoride film is prepared as follows. A nickel vessel containing the aluminum plate (2 sheets) and graphite powder (1 g) was placed in a nickel reactor, followed by pumping at room temperature. After heating to a reaction temperature, the reactor was filled with fluorine gas of 1 atm. During the reaction, the reactor was rotated at 2 min^{-1} by a motor with a mechanical seal. The fluoride film so prepared was analyzed by contact angle measurements (at 30 °C), X-ray diffractometry (by Cu$K\alpha$), X-ray microanalyzer, IR and ESCA spectroscopies.

Resuts

Contact Angle of a Water Drop on the Fluoride Film. A fluoride film having a high contact angle (Fig. 1) and smooth surface was obtained by the reaction performed at 450—500 °C. It was very difficult to prepare such a film below 400 °C, and aluminum plate was often deformed at higher temperature of 550—600 °C.

Figure 2 is the change of a contact angle on a surface film of aluminum as a function of reaction time. A

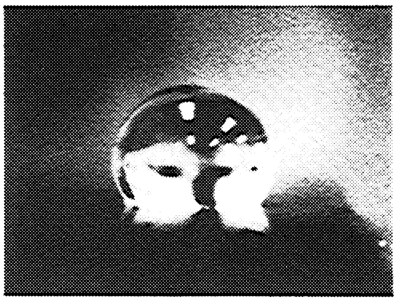

Fig. 1. Contact angle of water drop (θ) on the graphite fluoride film.
θ=125°, Preparation of the film: 500 °C, 24 h.

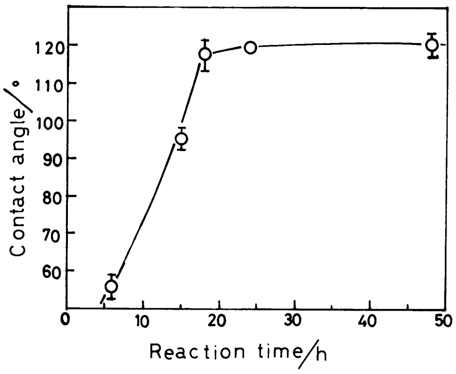

Fig. 2. Contact angle of water drop on surface film of aluminum as a function of reaction time.
Reaction temperature: 500 °C.

fluoride film with a contact angle of 120 ° was prepared by the reaction for 20 h. The change in the surface appearance with reaction time is shown in Fig. 3. At the beginning of a reaction, a white amorpous substance of 50—100 μm in thickness and with a low contact angle was formed on the surface of the aluminum (Fig. 3a). It consisted of aluminum fluoride and fluorinated aluminum carbide, as shown later from X-ray diffraction pattern and ESCA spectra. As the reaction progressed, a black part began to appear as shown in Fig. 3b, being a very thin film (<10 μm) with a higher contact angle. After 20 h, the film formation was completed. The aluminum surface was covered by a thin black film of 3—8 μm with a contact angle of 127.5 ° (Fig. 3c).

Figure 4 shows the change of the contact angles of fluoride films prepared at different temperatures with the holding time in air. The contact angle gradually decreased from 120 ° to 85—95 ° during 45 d. This might be due to reaction with moisture in air or the

† 1 M = 1 mol dm^{-3}

(a)

(b)

(c)

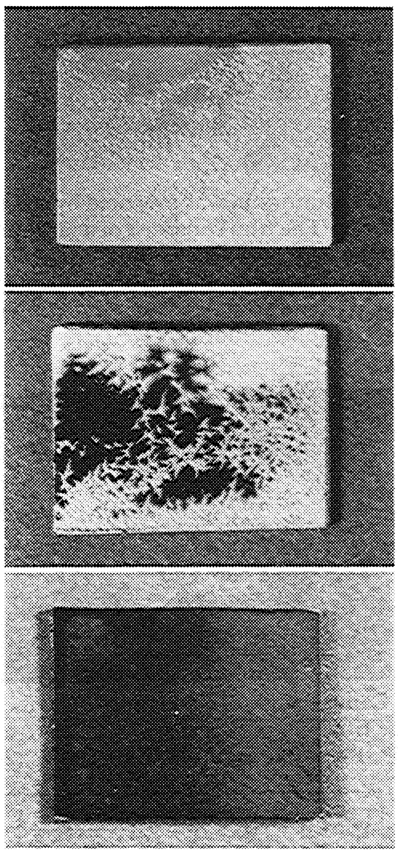

Fig. 3. Change of surface film of aluminum with reaction time.
a) Reaction: 12 h, 500 °C. Contact angle: 30.5 °. Film thickness: 50—100 μm. b) Reaction: 18 h, 500 °C. Contact angle: 89 ° (black part), 50 ° (white part). c) Reaction: 24 h, 500 °C. Contact angle: 127.5 °. Film thickness: 3—8 μm.

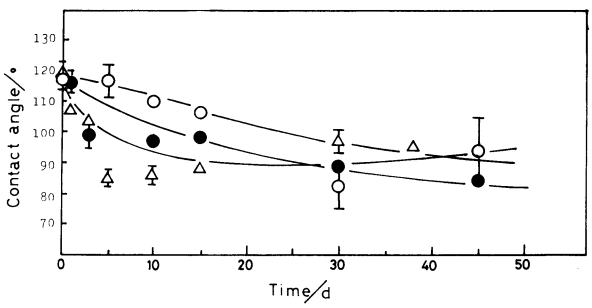

Fig. 4. Change in contact angle of water drop on surface film of aluminum as a function of time.
○: 500 °C, 18 h, ●: 500 °C, 24 h, △: 500 °C, 48 h.

water drop used in the contact angle measurement. The decrease in the contact angle was larger for a fluoride film wetted by a water drop on the contact angle measurement than for that only left in air.

IR Spectra. Figure 5 shows the IR spectra (ATR) of the fluoride films. Figure 5a was measured several days after preparation of a film having a contact angle of 92—133 °. A broad absorption observed around 1220 cm^{-1} is assigned to a CF stretching vibration (1215 cm^{-1}) and CF_2 symmetric and asymmetric vibrations (1380, 1110 cm^{-1}) of graphite fluoride.[3] A strong absorption around 600 cm^{-1} indicates aluminum

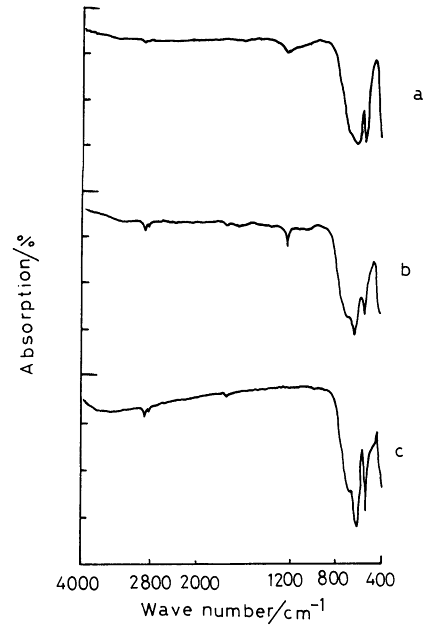

Fig. 5. IR spectra (ATR) of surface film of aluminum.
a: θ=92—133°, reaction: 500 °C, 24 h. b: θ= 114→70°, reaction: 450 °C, 48 h. c: θ=Spread, reaction: 550 °C, 72 h.

fluoride. It was found from the intensity of each absorption band that the fluoride film contained a large amount of aluminum fluoride and a small amount of graphite fluoride. Figure 5b was obtained for a sample whose contact angle decreased from 114 ° to 70 ° by the reaction with moisture and water drops. In addition to a sharp absorption of the CF stretching vibration, two absorptions for carbonyl groups appeared around 1600 cm^{-1} and 2800—3000 cm^{-1}, respectively. The decrease of contact angle is probably because CF_2 group was removed by the reaction with water and the carbonyl groups were newly formed. Only carbonyl groups were found for a film on which water drop spread (Fig. 5c).

X-Ray Diffraction Pattern. An example of the X-ray diffraction pattern of a fluoride film in given in Fig. 6 where α and γ-AlF_3 and metallic aluminum were observed. No diffraction line of graphite fluoride was detected probably because of the very thin film.

X-Ray Microanalysis. Figure 7 is the elemental analysis of a cross section of a fluoride film. It was

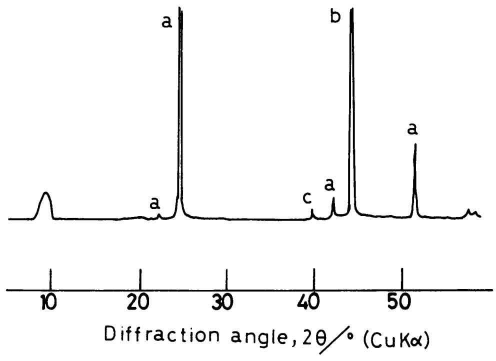

Fig. 6. X-Ray diffraction pattern of surface film of aluminum.
a: α-AlF_3, b: Al, c: γ'-AlF_3
Reaction: 500 °C, 48 h.

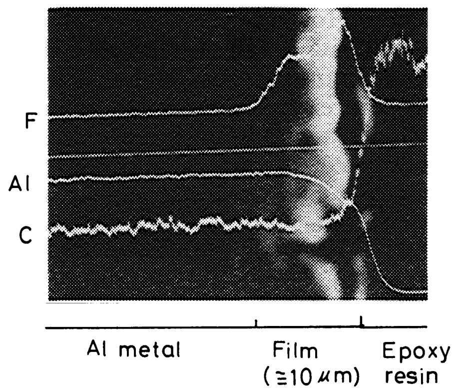

Fig. 7. Elemental analysis by X-ray microanalyser Reaction: 500 °C, 24 h.

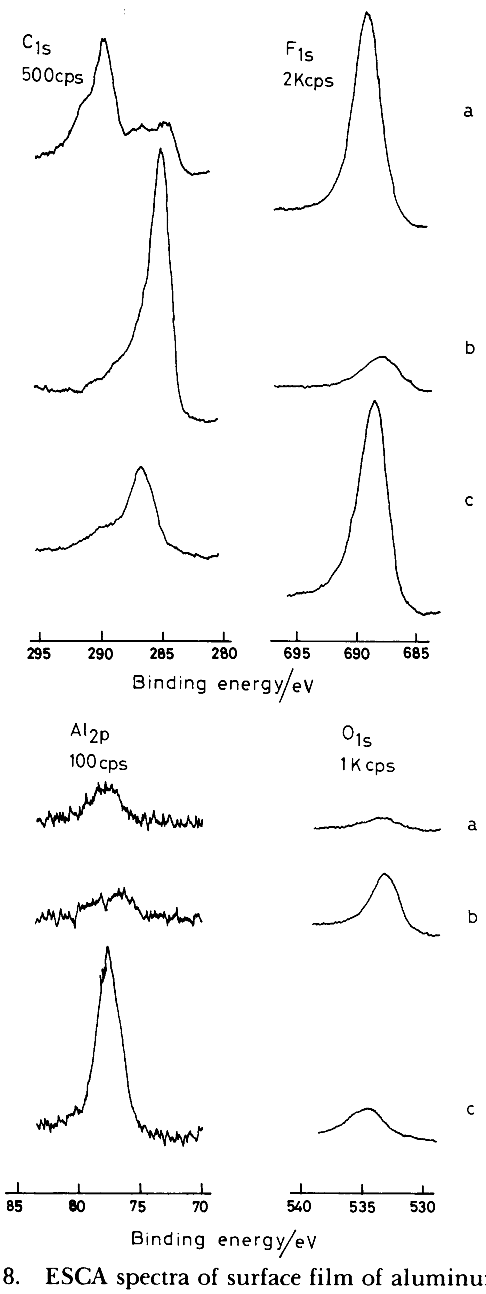

Fig. 8. ESCA spectra of surface film of aluminum. a: θ=106.3°, reaction: 450°C, 24 h. b: θ=121.3→83.7°, reaction: 475 °C, 48 h. c: θ=81.0°, reaction: 550 °C, 24 h.

found that the film contained large amounts of fluorine and aluminum, and a small amount of carbon. The amounts of fluorine and carbon increased toward the surface of the film while that of aluminum gradually decreased. It is surprising that no oxygen was detected in the film.

ESCA Spectra. ESCA provides the information on a chemical bond of a solid surface. Figure 8a is the spectra of a film with a high contact angle. C_{1s} spectrum had two peaks at 290.0 and 292.0 eV corresponding to CF and CF_2 groups of graphite fluoride, respectively. The position of the F_{1s} peak is the same as that of graphite fluoride. The peak for Al_{2p} was found at 77.9 eV slightly higher than that of aluminum fluoride. O_{1s} peak was observed although the peak intensity was extremely low compared with that of the F_{1s} peak. Figure 8b was obtained for a film after its contact angle decreased from 121.3° to 83.7°. The C_{1s} and F_{1s} peaks corresponding to CF and CF_2 groups were decreased remarkably by the decomposition of thin graphite fluoride layers. The C_{1s} peak, indicating hydrocarbon compounds, appeared strongly at 285.0 eV, and the F_{1s} peak was shifted to 688.0 eV near that of aluminum fluoride. On the other hand, the intensity of O_{1s} peak increased considerably probably because of the formation of carbonyl groups. Figure 8c shows the spectra of a film with a low contact angle. It seems that this sample was in the course of the formation of graphite fluoride film as shown in Fig. 3a. The C_{1s} spectrum had a strong peak at 286.7 eV which was consistent with that of aluminum carbide, Al_4C_3, fluorinated by fluorine gas at 500 °C. The peak around 290 eV indicating graphite fluoride had a low intensity. Fluorinated aluminum carbide gave an F_{1s} peak at the same position, 688.7 eV, as that of graphite fluoride. This result suggests the formation of an Al–C–F bond. The high intensity of the Al_{2p} formation of an Al–C–F bond. The high intensity of the Al_{2p} peak would be due to fluorinated carbide and aluminum fluoride since the graphite fluoride layer was not formed appreciably. The O_{1s} peak was found at a higher posi-

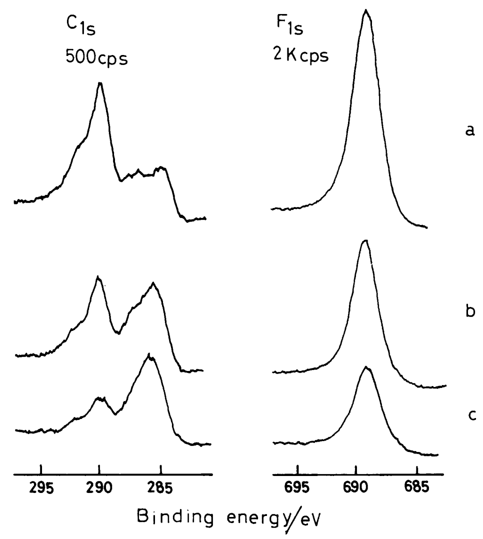

Fig. 9. ESCA spectra of surface film of aluminum. a: Film surface, b, c: polished by an emery paper.

tion than that of aluminum oxide probably because of the formation of fluoride oxide. Figure 9 is the spectra of the inside of a film obtained by polishing with an emery paper. Graphite fluoride decreased toward the inside of the film, while the peak of the fluorinated carbide at 286.7 eV increased. The latter was also decreased by further polishing and the peak for the aluminum substrate appeared.

Discussion

Structure of the Fluoride Film. From the results obtained by X-ray diffractometry, IR and ESCA spectroscopies, it was found that the fluoride film consisted of a large amount of aluminum fluoride and thin graphite fluoride layers around the film surface. The CF group comprised in graphite fluoride and fluorinated aluminum carbide rapidly decreased from the surface of the film into the inside. ESCA spectra suggested that graphite fluoride layers were chemically bonded to aluminum metal through the fluorinated aluminum carbide.

The contact angle of the water drop on the film was around 120°, which was almost equal to that for graphite fluoride prepared from flaky natural graphite.[2] The contact angle gradually decreased from *ca.* 120° to around 90°. This was explained by the IR spectra of the films. As shown by ESCA spectra, graphite fluoride on the surface of the fluoride film would have a chemical bond with the aluminum substrate through the fluorinated aluminum carbide having an ionic nature. Aluminum carbide with an ionic bond is easily decomposed by reaction with water. There would be many CF_2 groups around the edge of the graphite fluoride layer of the film as well as graphite fluoride powder. It is expected that these CF_2 groups are slightly ionic in chemical bond, being different from the CF_2 group with a covalent bond in graphite fluoride itself. For this reason, the CF_2 groups of the fluoride film would be decomposed by the reaction with moisture in air or water drop. As a result, the carbonyl groups were formed on the surface of the film.

No oxygen was detected on elemental analysis by X-ray microanalyzer. In this case, the analyzed depth is about 1 μm and the detection limit of oxygen is 0.1%. The analyzed area was a cross section of a fluoride film (≅10μm) bonded to aluminum substrate as shown in Fig. 7. In the case of ESCA, the analyzed area is the sample surface itself ($2\times10^{-5}\,m^2$), and the analyzed depth is limited by the mean free path of the photoelectron in the solid; this is only several nanometers. Oxygen adsorbed on a sample surface is therefore easily detected by ESCA measurement. For example, almost the same amount of oxygen is detected for the surface of poly(tetrafluoroethylene) which does not contain oxygen in the structure. Accordingly, it can be said that the fluoride film contains almost no oxygen.

Reaction of Aluminum with Graphite Fluoride and Fluorine. The attempts to prepare a pure aluminum fluoride film on the surface of aluminum were made by electrochemical fluorination in hydrogen fluoride and by reaction with fluorine gas at a high temperature. However, they were unsuccessful because oxygen contained in the surface oxide layer of aluminum could not be removed by such fluorination reactions.[4] Since aluminum oxide is very stable, it is very difficult to reduce aluminum oxide below 600°. The reduction of an oxide film on aluminum would be attained only by chemically active species such as radicals. Graphite fluoride somewhat decomposes at 450—600 °C, giving CF_2 radicals[5–7] with life time of the order of second.[8–10]

$$2(CF)_n \longrightarrow n\mathrm{C(amorphous)} + xCF_2 + yC_2F_4 \tag{2}$$

The products obtained by thermal decomposition of $(CF)_n$ are amorphous carbon, unsaturated fluorocarbons (C_2F_4, C_3F_6) and saturated fluorocarbons (CF_4, C_2F_6, C_3F_8).[5–7] It was reported that C_2F_4 does not decompose to CF_4 below 700 °C.[11] The saturated fluorocarbons are therefore regarded as 2nd order products of CF_2 radicals. It is then expected that the CF_2 radical decomposes to a carbon radical and CF_4 by the disproportionation reaction.

$$2CF_2 \longrightarrow C^* + CF_4 \tag{3}$$

C*: carbon radical

This carbon radical would reduce the oxide layer of aluminum.

$$Al_2O_3 + 3C^* \longrightarrow 2Al + 3CO \tag{4}$$

$$CO + F_2 \longrightarrow COF_2 \tag{5}$$

Metallic aluminum Al* would immediately react with fluorine gas, CF_2 radical, carbon radical C* and/or graphite fluoride.

$$Al^* + 3/2F_2 \longrightarrow AlF_3 \tag{6}$$

$$Al^* + CF_2 \longrightarrow Al\text{–}CF_2 \tag{7}$$

$$Al^* + C^* \longrightarrow Al\text{–}C \tag{8}$$

$$Al^* + (CF)_n \longrightarrow Al\text{–}(CF)_n \tag{9}$$

The product of reactions (7) and (8) would further react with radical species and/or graphite fluoride to produce the fluoride film with graphite fluoride.

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