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Further investigation on the thermal decomposition of aluminium dialkylamides

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Both dimethylamino- (I) and diethylamino-alane dimers (II), $[(R_2N)_2AlH]_2$ (I, R=Me; II, R=Et) decompose above 800° C under a few hundred Pa of hydrogen to dark greyish, hard (Vickers hardness larger than 2000), oxidation-resistive and oxidation-protective deposits which are tentatively identified as Al_5C_3N. The deposits are stable to moisture and diluted hydrochloric acid in contrast to those obtained below 800° C, but they easily dissolve in sodium hydroxide solution at room temperature evolving a gas. The deposits on a stainless steel substrate adhere strongly to the substrate and remain so on rapid heating and cooling. The electrical resistivity of the deposits is in the range 10^2 to 10^4 Ω cm.

1. Introduction

In a previous paper [1], the relatively hard and oxidation-protective coating films obtained at 300 to 500° C by thermal decomposition of aluminium dialkylamides were described. However, the coating films are unfortunately sensitive to water, and so the films easily peel off the substrate plate after standing in moist air for 2 to 3 days. Thus, the low temperature deposits have only a limited practical use despite their excellent properties such as hardness and oxidation-protection. In order to obtain a more stable deposit, the high temperature decomposition of aluminium dialkylamides was re-examined.

2. Experimental procedure

The complexes, bis(dimethylamino)alane dimer $[(Me_2N)_2AlH]_2$, (I, m.p. 67 to 69° C, b.p. 83° C/ 19.99 Pa, containing 6% $[(Me_2N)_3Al]_2$ as an impurity) and bis(diethylamino)alane dimer $[(Et_2N)_2AlH]_2$, (II, b.p. 88 to 89° C/5.33 Pa) were prepared according to the literature method [2], and were used for the decomposition reaction after identification by infrared (i.r.) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy [3] and mass spectroscopy.

The complex transport system has been already described [1]. The chemical vapour deposition (CVD) apparatus employed a horizontal, 40 mm internal diameter (i.d.) quartz tube reactor with a graphite susceptor (55 mm x 23 mm x 18 mm), the front side of which was tilted at an angle of about 20° relative to the normal direction of the gas stream. The susceptor was heated by a radio frequency (RF) power supply (400 kHz, maximum output 5 kW). The vapour of the complex (I or II) was saturated with hydrogen (purified by active copper and phosphorous pentoxide) at a suitable temperature (60 to 90° C) and was introduced at a reduced pressure on to a substrate (stainless steel, 15 mm x 5 mm) mounted on the front side of the susceptor. The temperature of the susceptor was measured using an optical pyrometer, but the substrate temperature was not measured. Therefore, the deposition temperature cited in the text is the susceptor temperature.

The substrates were abraded and polished with an emery paper (No. 1200) and washed with water and distilled acetone, successively, in an ultrasonic bath for about 10 min. They were then treated under a hydrogen atmosphere (a few hundred Pa) at about 900° C for 10 min in the reaction furnace before the introduction of the complex.

The deposits on the substrate were examined

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by X-ray diffraction, Auger electron spectroscopy (AES), electron probe microanalysis (EPMA), X-ray photoelectron analysis (ESCA), visible and infrared spectroscopies. The Vickers hardness and electrical resistivity of the deposits were also measured by conventional methods.

3. Results

3.1. Effect of the deposition temperature on the deposits

The complexes used in this study were very stable thermally [1, 3], and did not decompose appreciably below 300° C. Above about 300° C the complexes began to decompose to produce the deposits. At about 600° C the deposition rate became very fast. The deposits in these temperature regions were coloured brown or dark brown and were unstable to moisture. After standing for a few days in moist air the deposits changed their colour to pale yellow or white and peeled off the substrate. The stability of the deposits above 700° C increased with increasing deposition temperatures, and above 800° C very stable deposits were obtained. No change in appearance was found even after standing in moist air for several months.

The appearance of the as-grown deposits also varied with deposition temperature, and the deposits above 800° C were coloured dark grey and had a metallic luster after polishing. As will be described in a later section, the deposits above 800° C had a large electrical conductivity. Both alane complexes (I) and (II) produce very similar deposits.

The temperature dependences of the deposition yields in the case of complexes (II) and (I) are shown in Figs 1 and 2, respectively. In the case of complex (II) the deposition yield decreased sharply at 850 to 900° C, and above 900° C no deposits were found despite the weight increase of the substrate after deposition reaction. The weight increase may be ascribed to reaction of the substrate with a carbon species which was generated by an up-stream decomposition of the complex. A glow discharge which was observed at a high plate-voltage of the RF power supply (> 900° C, 3.6 kV) may accelerate the up-stream decomposition. In the case of complex (I), a similar relationship between the temperature and the deposition yield was observed (Fig. 2). An apparent higher deposition yield in the case of the complex (I) compared with complex (II) was largely due to the higher vapour concentration of complex (I), since the melting point of (I) restricts the lower limit of saturation temperature. Nevertheless, the higher stability of complex (I) compared with (II) may contribute partly to the difference in the temperature–yield profiles of Figs 1 and 2.

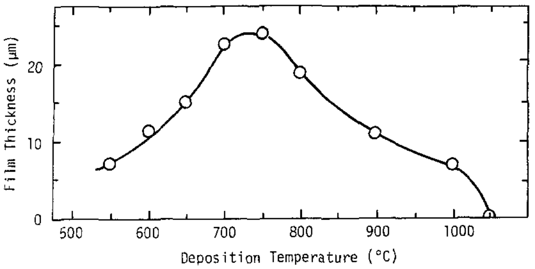

Figure 2 Temperature dependence of deposition yield: complex, I; saturation temperature; 60° C; deposition time, 30 min; carrier gas H_2, 0.06 ml sec^{-1} (for saturation) + 0.78 ml sec^{-1} (for bypass); pressure 330 Pa.

The deposition yields increased linearly with the reaction time as shown in Fig. 3. Since the thickness of the deposits was directly proportional to the reaction time for the initial time, and since the deposition rate was independent of the

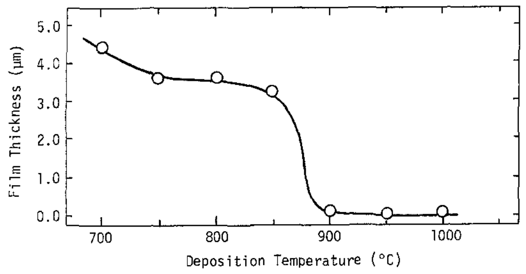

Figure 1 Temperature dependence of deposition yield: complex, II; saturation temperature, 90° C; deposition time, 30 min; carrier gas H_2, 0.4 ml sec^{-1} (for saturation) + 0.3 ml sec^{-1} (for bypass); pressure, 333.25 Pa.

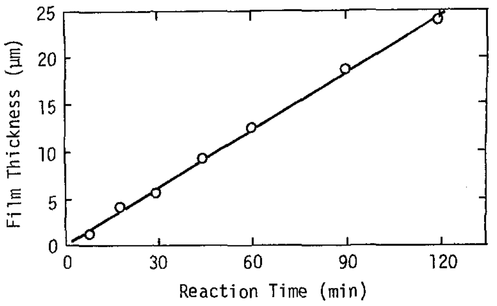

Figure 3 Time dependence of deposition yield: complex, II; saturation temperature, 90° C; deposition temperature, 800° C; carrier gas H_2, 0.4 ml sec^{-1} (for saturation) + 0.3 ml sec^{-1} (for bypass); pressure 330 Pa.

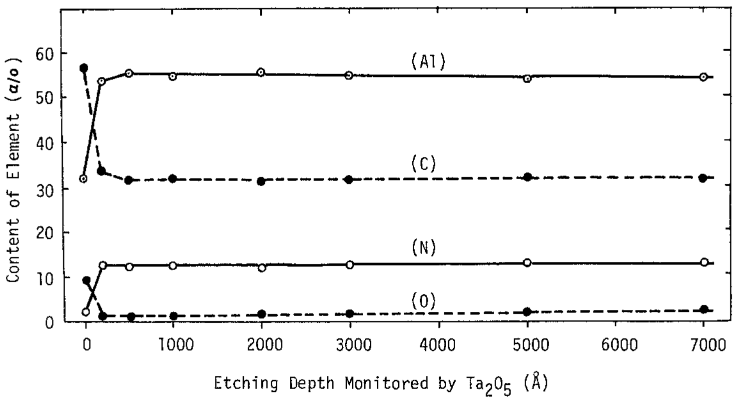

Figure 4 Content of elements (in at %) determined by AES for the deposit obtained for complex (II) at 800° C.

substrates such as SiO_2, Al_2O_3 and graphite-plate, it can be assumed that the substrate surface has little catalytic effect on the film growth. There is some disagreement between the data of Figs 1 and 3. These experiments were made under the same conditions of flow rate of carrier gas and saturation temperature. After many runs, however, the complex partially decomposes by a reaction with traces of moisture or oxygen in the carrier gas to yield a non-volatile compound which can lower the vapour pressure of the complex. This reduction in the vapour concentration of the complex after many runs may be an origin of the disagreement.

3.2. Identification of the deposits

The deposits obtained above 800° C are dark-greyish, condensed films which are very hard, having a metallic luster after polishing and a moderate electrical conductivity even at room temperature (*vide infra*). These properties are very different from those known for aluminium nitride or carbide which were expected to be deposited by the thermal decomposition of the aluminium dialkylamides.

X-ray diffraction did not aid the identification of the deposits because no diffraction peak was obtained. Even after annealing at 1200° C *in vacuo* no distinct diffraction peaks were found. When the deposits were heated in air at 1400° C for 45 min, peaks which may be assigned to AlN (1 0 0), (0 0 2), (1 0 1) and (1 0 2) diffractions were observed along with those of aluminium oxide.

In EPMA of the deposit (8 μm thick) on a molybdenum plate only an AlKα line was observed. The intensity ratio k_{Al} of the AlKα line to that of the aluminium metal reference was 0.63 under the same measuring conditions (30 kV, 30°). The k_{Al} was not directly equal to the aluminium content C_{Al} of the product and is generally described by the equation

$$C_{Al} = G^{X}_{Al}(k) \cdot k_{Al} \qquad (1)$$

where $G^{X}_{Al}(k)$ is a correction factor depending on the type and concentration of co-existing element X and is a function of the intensity ratio k. This correction factor can be computed by considering the influence of the co-existing element (matrix), namely, absorption of emitted X-rays, fluorescence and the atomic number. A great many values of $G^{X}_{Y}(k)$ and $G^{Y}_{X}(k)$ have been computed for common binary X–Y mixtures. They are compiled in "Diagrams and Tables for Quantitative Electron Probe Microanalysis" [4]. By considering the probable product to be carbide or nitride and by using the corresponding correction factors $G^{C}_{Al}(k = 0.63) = 1.10$, and $G^{N}_{Al}(k = 0.63) = 1.18$ [4], the aluminium content C_{Al} was evaluated from the intensity ratio $k_{Al} = 0.63$ and Equation 1 was evaluated as 69 and 74% for the carbide and nitride, respectively. If the product is a carbonitride, the content may be in the range 69 to 74%.

The composition of the deposit was determined using AES and the results are shown in Fig. 4 as a function of etching depth. Below 200 Å from the surface the product has a constant composition $Al_5C_{2.9}N_{1.1}O_{0.1}$. There has been concern about the accuracy of the quantitative analysis using AES. However, the aluminium content of 71.9% calculated from the above composition is well in the range obtained by EPMA. Moreover, the composition corresponds to a 1 : 1 solid solution of the carbide (Al_4C_3) and the nitride (AlN). The homogeneous carbonitride Al_5C_3N is already known [5, 6]. Therefore, it can be concluded that the deposits obtained in this study were the carbonitrides which have a composition Al_5C_3N. The oxygen content was as low as 1.2%.

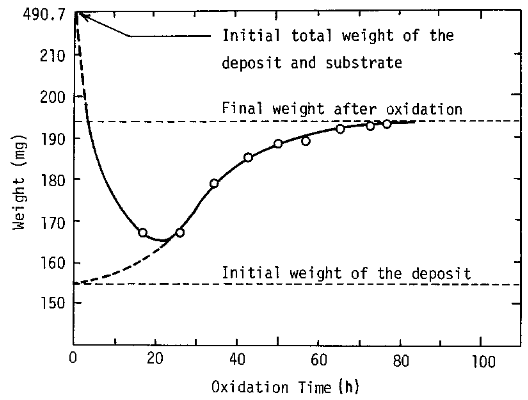

Figure 5 Oxidation of the deposit (154.8 mg) obtained on a graphite plate (335.9 mg) at 800° C and weight increase observed during oxidation in air at 1000° C.

ESCA also shows the presence of aluminium (Al 2s, 118.8; 2p, 74.2 eV), carbon (C 1s, 285 eV), nitrogen (N 1s, 396.8 eV with a shoulder at 398.8 eV) and oxygen (O 1s, 531.5 eV with a very weak shoulder around 530.5 eV). All binding energies of the corresponding atoms are cited from the values observed after 30 min sputter-etching The relative peak intensities (by peak areas) of the elements in the spectrum were 1 (Al 2s): 0.78 (Al 2p): 2.3 (C 1s): 0.70 (N 1s): 4.15 (O 1s), which are very different from those expected from AES. In particular, the O 1s peak is too intense to be assigned to the oxide ion which was present as an impurity. Moreover, the binding energy observed for the O 1s was higher by a few electron volts than that of the oxide state (*ca.* 530 eV) and was close to that of molecular oxygen. The very weak shoulder observed at about 530.5 eV, therefore, may be assigned to the oxide impurity.

There was no chemical shift in the C 1s peak energy, suggesting that the carbon exists in the elemental state. If so, the product should be identified as the nitride and have a composition near Al_5N as supposed from the intensity ratio of Al 2s to N 1s [7]. It is known that aluminium nitride is insoluble in metallic aluminium [8]. Moreover, the chemical shift of Al 2s does not correspond to Al(0) but rather to Al(III). Therefore, it is reasonable to assume that carbon exists at least partly as the carbide.

A deposit (75 μm thick, 154.8 mg) on a graphite plate was oxidized in air at 1000° C (only one side of the plate was coated). The weight change observed is recorded in Fig. 5. After a rapid initial decrease in weight due to oxidation of the graphite plate itself, the weight increased very slowly with oxidation time with a colour change from dark grey to blue and subsequently pale grey to white. Even after 80 h some greyish areas still remained. At this stage the ash weighed 193.1 mg and was identified as alumina by the X-ray diffraction pattern. The weight difference before and after oxidation suggests that the aluminium content was 66.7%. Considering the presence of the still unoxidized portion, the content cited above may be a minimum one. The ash due to the graphite itself was negligible. Therefore, this result supports the above data of EPMA and AES well. From this oxidation experiment it also may be concluded that the deposit is highly oxidation-resistive similar to the low temperature deposits [1].

3.3. Properties of the deposits

3.3.1. Electrical and optical properties

The deposits at temperatures lower than 700° C had an electrical resistivity of $10^{11\text{ to }14}\ \Omega$ cm, but the resistivity decreased with increasing deposition temperature, reaching $10^2\ \Omega$ cm at 900° C. Normal aluminium nitride or carbide and probably carbonitride are electrical insulators. Thus the high electrical conductivity of the high temperature deposits may be partly due to the presence of elemental carbon dispersed homogeneously in the bulk. However, the resistivity has a tendency to decrease when the deposit at 750° C was thermally retreated at 900° C under a few hundred Pa of hydrogen for 10 to 30 min.

From the temperature dependence (temperature range 10 to 200° C) of resistivity of a deposit at 750° C, the activation energy of conduction was calculated as 25.5 kcal mol^{-1} (1.1 eV). On the other hand, the visible absorption spectrum of the deposits at 650° C on a silica glass showed a relatively sharp absorption edge at 350 to 400 nm, corresponding to the optical band gap of 3.1 eV.

The infrared absorption spectrum of the deposit obtained using a KBr disc at 650° C was very similar to that of the low temperature deposits [1], and has a strong, broad band at 610 to 650 cm^{-1} which was somewhat different from the data for aluminium nitride (710 cm^{-1}) [9]. Although the deposits at much higher deposition temperatures could not be examined, there seemed to be no essential difference with changing deposition temperature as far as the infrared spectrum was concerned. Perfect elimination of the organic fragment can take place even at 400° C. Therefore, the conversion of a metastable compound to a

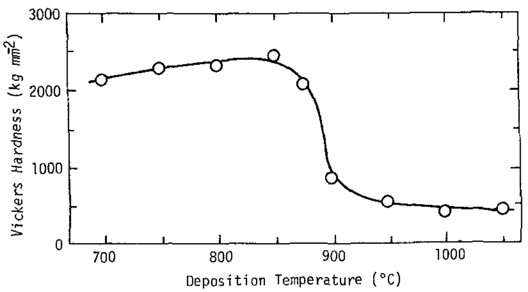

Figure 6 Effect of deposition temperature on the hardness of the deposits; complex, II; deposition conditions are the same as in Fig. 1.

stable one by deposition temperature is attributed to a solid rearrangement of the deposits.

3.3.2. Hardness of the deposits and their adhesiveness to the substrate

Vickers hardness (H_v) of the deposits obtained on a stainless steel substrate is shown in Figs 6 and 7 as a function of the deposition temperatures. It is worth noting that the hardness (at 100 g load) is greater than 2000, reaching a maximum value of 2800 when complex (I) was used as a starting compound. The observed hardness was higher than that known for aluminium nitride (Knoop hardness $H_k = 1225$ [10]; H_v nearly equals $1.2 H_k$ [11], then $H_v = ca.\ 1500$), and is close to the hardness of aluminium oxide ($H_v = 3000$ [11]). The hardest deposit from complex (II) can be obtained at 800 to 850° C and from complex (I) at about 900° C.

Above 800° C very adherent and dark greyish films can be obtained without any crack in the films. However, in films grown at temperatures lower than 800° C, many cracks have been found and the films were unstable in air, as mentioned before. Therefore, it can be concluded that the lowest temperature limit for the deposition of hard and stable films is about 800° C at a deposition rate of 0.1 to 0.5 μm min^{-1}, although the limit may be lowered further by selecting a slower deposition rate. The deposits on stainless steel above 800° C can adhere tightly to the substrate. Even if the coated sample was heated rapidly in the flame of a burner above 900° C and subsequently quenched in water, the film did not peel off the substrate. The deposits also stand up well against a so-called hammer-test except for partial chipping of thick layers.

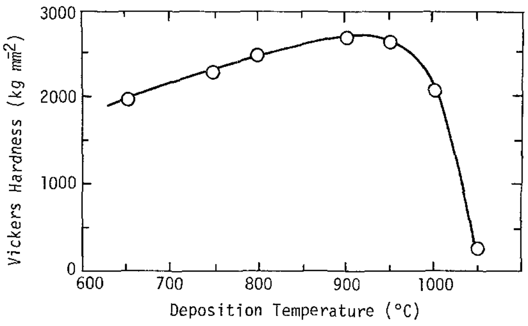

Figure 7 Effect of deposition temperature on the hardness of the deposits; complex, I: deposition conditions are the same as in Fig. 2.

In order to obtain further information on the deposition state, Meyer indices [12] were examined which relate the applied loads to the diagonals of indentation. The indices of the deposits at 750 to 850° C are in the range 1.6 to 1.7. The higher temperature deposits tend to have lower indices. When a deposit at 800° C was heat-treated at 900° C for 30 min, the index increased to 1.9, suggesting that some heat treatment of the deposits around 800° C is required to improve the mechanical properties.

3.3.3. Chemical properties

When the deposits were exposed to air at high temperatures, the colour of the surface changed as described above. At the same time the electrical conductivity of the surface disappeared, but the original greyish colour with the metallic luster and the electrical conductivity were restored by polishing. Therefore, the oxidation stability of deposits can be attributed to the formation of some protective layer, probably a very thin oxide layer which could not be found by microscopic examination of the cross-section. The stainless steel substrate which was covered with a 10 μm thick film can resist oxidation in air at 1000° C for 10 h. The deposits were stable in dilute hydrochloric acid in contrast to the low temperature deposits, but are easily decomposed by sodium hydroxide solution at room temperature, evolving a gas and leaving a small quantity of black residue, probably carbon.

4. Discussion

As described in Section 3, the deposits obtained through our study can be identified as a carbonitride Al_5C_3N, which was very hard, highly oxidation-resistive and oxidation-protective. Increase in the deposition temperatures indeed improved the stability to moisture. Considering both these excellent properties of the deposits and their good adherence to stainless steel substrates, they may be expected to have an application in wear-resistant or oxidation-protective coatings.

Although our starting compounds seem to be less common, they can be prepared easily, economically and on a large-scale by a direct reaction of metallic aluminium with the corresponding dialkylamine in hydrogen at a moderate temperature (150° C) and pressure (2.1×10^4 to 2.8×10^4 kPa) according to the convenient Kovar-Ashby process [3]

$$2\,\mathrm{Al} + 3\mathrm{H_2} + 4\mathrm{R_2NH} \rightarrow \underset{\text{(I and II)}}{[\mathrm{HAl(NR_2)_2}]_2} + 4\mathrm{H_2}.$$

Therefore, the process of obtaining a refractory aluminium compound can be extended to an industrial process if the process has any practical superiority.

Manasevit and co-workers reported [13] that in the $Me_3Al{-}NH_3{-}H_2$ system, aluminium nitride can grow epitaxially on various substrates. Our starting complexes, dialkylaminoalanes $(R_2N)_2AlH$, are different apparently from those in the Manasevit–Erdmann–Simpson process, but it is felt that both processes contain very similar vapour species especially at higher temperatures, considering the thermal stability of the complexes. Therefore, both processes should give similar deposits, but this is not so. In order to give a clear explanation for the difference, further investigation including mechanisistic study is required.

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