REACTION OF GASEOUS HYDROGEN FLUORIDE WITH ALUMINIUM AND ITS COMPOUNDS

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The reaction of metallic aluminium surfaces, aluminium oxides, hydrated oxides and sulphate with gaseous anhydrous hydrogen fluoride was studied at 470°C and pressures between 10 and 100 torr. The complementary analytical techniques of X-ray induced photoelectron spectra, X-ray and electron diffraction, and electron microscopy were used for identifying the (frequently unexpected) products.

1. Introduction

Metallic aluminium acquires extremely rapidly at room temperature in ordinary air a superficial layer of some 10 Å thickness of a hydrated oxide, which is known in some cases not to grow significantly when the metal is kept for 50 years. Since this layer-thickness has the same order of magnitude as the mean escape-width of photoelectrons [1] with a kinetic energy slightly above 1000 eV (and not having suffered inelastic collisions) the photoelectron spectrum induced by soft X-rays shows two distinct sets of AI 2s and Al 2p signals [2] separated by 2.8 eV, the component at lower ionization energy I (corresponding to the bulk metal) being about half as intense as the component at higher I (corresponding to the surface oxide).

In view of the complicated and interesting chemistry of aluminium fluorides, and the expected large chemical shift of I [2,3] it was felt useful to study the reaction of this surface with HF (and various kinetic aspects [4] have been investigated in greater detail) and to compare the photoelectron spectra of surface films with definite compounds.

2. Experimental

The various aluminium oxides were prepared in the Neuhausen laboratory according to known methods [5-8]. Commerical hydrogen fluoride (about 99.5%) was used after thorough purification by fractional distillation [9]. In the following, the gaseous phase is called HF in spite of a certain extent of oligomerization. The metals used for the apparatus were Inconel and Monel alloys, nickel, stainless steel, copper, and also transparent teflon (FEP, Du Pont). The composition of the gaseous phase in the reactor was monitored with a quadrupole mass spectrometer (Balzers QMG 311) with a cross beam analyzer system. The gaseous anhydrous HF was introduced into the reactor at constant pressure after the sample had been heated until a constant reaction temperature had been reached. The pressure was measured with a capacitor Baratron vacuum gauge.

The photoelectron spectra were obtained with a Varian IEE-15 instrument equipped with a magnesium anti-cathode emitting a high intensity of 1253.6 eV photons. The instrument can be calibrated, e.g. with the strong Au 4f signals of metallic gold with I^* (rel-

ative to the Fermi level) = 83.8 and 87.5 eV, in which case hydrocarbons on the surface of the samples show $I^*(C 1s)$ close to 285 eV. However, in the case of nonconducting samples [2,10] we have serious reasons to invert this procedure, and define I (relative to vacuo) of typical hydrocarbons to be 290 eV, and we introduce the two quantities C_{st} and C'_{st} as the differences between 290 eV and the lower and higher value, respectively, recorded for $I^*(C \ 1s)$. We believe that a good approximation to the I relative to vacuo is the value I' corrected for charging effects by adding C'_{st} to the observed I^* , and that the quasi-stationary positive potential of the sample is close to $\partial = (C_{st} - C'_{st})$ which can be as high as 5 eV (with the Varian instrument) for highly isolating fluorides. Actually, the greater uncertainty in I' occurs when ∂ is below 1.5 eV with the undesirable result that the two C 1s signals must be separated by gaussian analysis. One of many arguments in favour of this interpretation is that the half-width of the higher of the two $I^*(C \ 1s)$ is only marginally broader than the other signal corresponding to uncharged hydrocarbon in the case of powdered samples distributed on one-sided scotch-tape. This shows a lack of excessive inhomogeneity in the positive potential maintained by the loss of photoelectrons. In table 1, the one-sided half-width $\delta(-)$ of the signal toward lower I^* is given.

It is possible [11] to establish relative intensities of photoelectron signals relative to fluorine 1s. The latter unit is colloquially called 1 w after Wagner [12] first attempting this approach (generally working within a factor 1.2 to 1.3). With 1253.6 eV photons, these intensities are 0.6 w for 0 1s, 2.0 w for Na 1s, 0.25 w for A1 2s and 0.30 w for Al 2p.

The electron diffraction pattern was obtained with a Philips EM 300 electron microscope, after separation of the thin films (200 to 1000 Å thick) with a methanolic bromine solution. The X-ray diffraction patterns were obtained with a Guinier powder camera (Nonius).

3. Results

The photoelectron spectra are given in table 1 and fig. 1. X-ray powder diagrams show clearly that α -Al₂O₃ (corundum) does not react, when exposed 20 min at 470°C to 30 torr HF. Nevertheless, the ESCA results show fluoride on the surface, about 2.4 F/Al considering the intensity of the signal having I'(Al 2s) = 125.1 eV. This value is about 1.5 eV too low to be attributed to a stoichiometric AIF₃. Such an interpretation is more likely with I'(Al 2s) = 127.6eV resulting from the transformation of amorphous aluminium oxides. The rather low $I'(F \ 1s) = 691.8 \text{ eV}$ may be due to a hydrated fluoride, or to a mixed hydroxide with strong hydrogen bonds. Anhydrous $Al_2(SO_4)_3$ is only transformed to a small extent (according to powder diagrams) to AIF₃ by HF treatment at 470°C, but the photoelectron spectra indicate 1.4 F/Al. The high $I'(F \ 1s) = 693.3 \text{ eV}$ and the large width $\delta(-) = 1.65$ eV are quite surprising; among the conceivable explanations are Franck-Condon broadening of a signal due to adsorbed HF (for which the gas has I = 693.8 eV) or to the rather unexpected formation of fluorosulphonate FSO_3^- .

It is possible to conclude from the results in table 1 and fig. 1:

(1) both anodized and electropolished aluminium show a very similar oxide form comparable to β -Al(OH)₃;

(2) the OH-groups present make hydrogen bonds with concomitant lower I'(F 1s);

(3) after the reaction with HF, only a low number (0.3 to 0.8 relative to Al) oxygen atoms remain in the surface;

(4) when anhydrous γ -AlF₃ is present, higher I'(F 1s) occur. This phase can be obtained by thermal decomposition of $(NH_4)_3$ AlF₆ [13] and by dehydration of AlF₃·3H₂O [14].

Electropolished aluminium reacting with HF is covered with a thin film composed of a mixture of γ -AlF₃ (with small amount of water in its holes) and α -AlF₃. The electron diffraction pattern was obtained with $\lambda = 37.54$ (Å mm) with MgO as calibrant.

In table 2, the thermal transformation and decomposition products of $(NH_4)_3$ AlF₆ and AlF₃ are given. Comparison with the surface measurements of treated aluminium samples helps to identify the major species present.

The values of $I'(N \ 1s)$ may be compared with the recent study [15] of the reduction of roughly neutral, 1 molar aqueous solutions of nitrate by metallic aluminium, where the major product having $I'(N \ 1s) = 405.2$ eV is the same as obtained by adsorption of NH⁴₄ by the oxide surface. This is a striking example of the general situation that the surface chemistry of metals is rather

Table 1 ESCA data of aluminiu	m oxides	and alumi	inium flv	lorides											
	I [*] (C1s)	$c_{\rm st}^{*}$	ş()	e	I'(Al 2s)	§ (-)	<i>I</i> '(Al 2p)	δ(-)	ľ(01s)	ş(-)	0/AI	<i>I</i> '(F 1s)	9 (-)	F/A1	Crystalline forms; X-rays and electron diffraction
α-Al ₂ O ₃	(285.7) 287.2	[2.8]	0.9 0.8	1.5	124.2	1.3	80.7	1.0	536.3	1.1	<i>6</i> 9	i	ł	1	α-Al ₂ O ₃
α-Al ₂ O ₃ + HF + 470°C	(285.3) 287.8	[2.2]	0.85 1.2	2.5	125.1 127.6	1.45 1.2	82.3	1.4	539.0 536.8	1.0 1.15	0.3 1.8	691.8	1.4	2.4	a-Al ₂ O ₃ no trace AlF ₃
7-M203	(285.3) 287.7	[2.3]	1.0	2.4	124.3	1.55	79.5	1.3	536.3	1.5	e	ł	I	l	β-Al ₂ O ₃
γ-Al ₂ O ₃ + HF + 470°C	285.3 288.0	[2.0]	0.85	2.7	126.7	1.55	82.0	1.35	538.3 535.8	1.25 1.25	0.42 0.32	692.2	1.55		a-Alf'3
β-Al(OH) ₃	286.0	4.0	0.8	1	125.1	1.25	80.3	1.0	537.8	1.35	ŝ	1	***	1	β-Al(OH) ₃ + α-Al(OH) ₃
β-Al(OH) ₃ + HF + 470°C	(285.6) 288.0	[2.0]	0.95	2.4	126.8	1.55	82.0	1.55	539.9 537.3	1.25 1.50	0.23 0.47	692.2	1.6	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	a-AlF ₃
α•Al(OH) ₃	285,9	4.1	0.8	l	124.7	1.15	79. 9	0.95	538.4	1.05	s	ł	ł	1	α-Al(OH) ₃ + (β-Al(OH) ₃)
α-Al(OH) ₃ + HF + 470°C	(285.4) 288.3	[1.7]	0.75	2.9	126.5	1.5	81.8	1.35	537.8 (540)	1.25 1.15	0.16 0.13	692.1	1.35		a-AlF ₃ (all rays are present)
Al-anodized a)	286.0	4.0	1.05	I	125.2	1.15	80.5	6'0	538.0	1.15	ŝ	t	ł	1	amorphous to elec- tron diffraction
Al-anodized + HF + 500°C a)	(285.4) 288.1	[1.9]	1.15 0.7	2.6	126.6	1.3	81.9	1.2	537.6	1.5	0.72	692.1	1.25	e	a-AlF ₃ clectron diffraction
Al-electropolished a)	285.6	4.4	6.0	I	125.3	1.25	80.4	1.4	537.2 536.2	1.1 0.95	3 1.15	ł	I	1	amorphous to elec- tron diffraction
Al-electropolished + HF + 470°C a)	(285.6) 287.8	[2.4]	1.2 1.25	2.2	126.3	1.25	81.6	1.1	537.4 535.1	1.2	0.2 0.05	691.9	1.25	го	γ -AIF ₃ + α -AIF ₃ + (AIF _X (OH) _{3-X})
Al ₂ (SO ₄) ₃ · 18 H ₂ O + HF + 470°C	286.0	4,0	1.0	1	127.3	1.55	82.4	1.4	539.0 536.5	1.3 1.15	5 1.1	693.3	1.7	1.8	Al ₂ (SO ₄) ₃ + (AlF ₃)
AIF 3 •3H 2O + 400°C	(284.9) 287.3	[2.7]	1.0	2.4	125.8	1.55	81.2	1.5	537.9	1.5	1.5	691.7	1.5	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	γ-AIF ₃ + (AIF _{1.65} (OH) _{1.35} • 0.375 H ₂ O
AlF ₃ , 90% anh.	(284.7) 287.4	[2.6]	0.8	2.7	126.6 (124.3)	1.25	81.9 (79.6)	1.05	537.0	1.5	2.5	692.2	1.2		α-AlF ₃ + (Al ₂ O ₃)
(NH ₄) ₃ AIF ₆ + 500°C	285.9 288.4	[1.6]	0.73	2.5	126.9	1.7	82.0	1.5	(540.1) 538.1	1.1 1.25	0.12 0.26	692.5	1.5	3	γ-AIF₃

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a) Measured without scotch tape.

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Fig. 1. Photoelectron data of aluminium oxide before (full-line) and after (broken) the reaction with anhydrous hydrogen fluoride. Dot-dash line of curves (a) represents $AI_2(SO_4)_3 \cdot 18 H_2O$ after the reaction with HF at 470°C, the spectra after the dehydration of $AIF_3 \cdot 3 H_2O$ at 400°C and the thermal decomposition of $(NH_4)_3 AIF_6$ at 500°C are given by (e) and (h) (full line). The curves representing AIF_3 90% anh. (dot-dash line) are given by (h).

different from the complexation in homogeneous solution.

It may be noted that the electron diffraction pattern of the thin aluminium fluoride film is essentially similar to the X-ray powder diagrams of the products of dehydration of $AlF_3 \cdot 3H_2O$ at 600°C and the thermal decomposition of $(NH_4)_3AlF_6$ at 500°C, whereas the photoelectron spectra are rather different. On

X-ray diagram	Compound, treatment	C'st	9	<i>I</i> '(F 1s)	δ(-)	F/Al	I'(Al 2s)	δ()	I'(N 1s)	δ(—)	N/AI
(NH ₄) ₃ AlF ₆	(NH4)3 AIF6, 30°C	4.1	0	692.0	1.3	6	125.4	1.2	407.4	1.1	3
NH4AIF4	(NH4)3 AIF6, 350°C	2.3	1.6	691.9 689.6	1.3 1.0	3 0.5	126.0	1.5	407.2	1.1	0.4
γ-AlF ₃	(NH4)3 AlF6, 420°C	1.6	3.1	692.5	1.5	3	126.9	1.6	(407)	1.1	0.1
γ -AlF ₃ + α -AlF ₃	(NH4)3 AIF6, 500°C	1.6	2.5	692.5	1.5	3	126.9	1.7	(407)	-	0.04
crystalline	AlF ₃ • 3H ₂ O, 30°C	3.0	2.2	691.5	1.3	3	125.9	1.4	-	_	-
amorphous	$AlF_3 \cdot 3H_2O, 30^\circ C$	2.8	2.3	691.8	1.4	3	126.2	1.5	-	_	_
γ -AlF ₃ + AlF _x (OH) _{3-x}	AlF3 • 3H2O, 400°C	2.8	2.4	691.7	1.5	3	125.8	1.6		_	
γ -AIF ₃ + α -AIF ₃ + Al ₂ O ₃	AlF3 • 3H2O, 600°C	3.0	2.2	692.7 (689.6)	1.3 1.3	3 1.5	124.5 (127.0)	1.4		_	-

Table 2 ESCA results for thermal decomposition products of $(NH_4)_3 AIF_6$ and $AIF_3 \cdot 3H_2O$

the other hand, the fluoride film obtained at 470°C on electropolished aluminium in the presence of HF, and $AlF_3 \cdot 3H_2O$ dehydrated at 400°C give similar photoelectron spectra.

We intend later to discuss the general problems of oxygen 1s signals of solids. It is seen in table 1 that oxide constituents with I'(O 1s) close to 538 and to 536 eV can co-exist in the same sample. We have frequently observed this behaviour in oxygen-containing compounds. It was recently pointed out in a study of silicates [16] that strongly bound water has I' close to 537.5 eV whereas the oxygen atoms bound to silicon generally have lower I', down to 536 eV. Both α -Al₂O₃ and γ -Al₂O₃ have I'(O 1s) = 536.3 eV, whereas oxygen in mixed fluorides can be almost 540 eV. With exception of a phosphate glass, a recent study [17] of borate, germanate, tellurite and mixed tungstate--phosphate glasses showed I'(O 1s) in the rather narrow interval 535.7 to 536.2 eV.

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