

The Metastable, Glasslike Solid-State Phase of HAIO and Its Transformation to Al/Al₂O₃ Using a CO₂ Laser

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Bis(*tert*-butoxyaluminum dihydride) (*t*BuOAlH₂)₂ decomposes on metal surfaces heated to 250 °C (Fe, Ni, Cu, Pt) and under reduced pressures of 0.01–0.1 atm with elimination of dihydrogen and isobutene to form a glasslike, amorphous film, which is composed of equimolar parts of hydrogen, aluminum and oxygen (elemental analysis, EDX analysis). The gases eliminated during this process were characterized by mass spectroscopy (H₂, isobutene) or by infrared matrix techniques (isobutene). The exclusive binding of hydrogen to aluminum is deduced from IR spectroscopy of the HAIO film and of its deuterated form DAIO. The HAIO layer (which shows no X-ray diffraction pattern), when heated to 450 °C or when exposed to a CO₂ laser, loses hydrogen and trans-

forms to an almost stoichiometric composite with nanoscale crystalline aluminum and aluminum oxide (Al/Al₂O₃) as ingredients. This transformation may be followed by IR spectroscopy, by ²⁷Al MAS NMR or by XPS, the latter showing different signals (Al, 2p electrons, Mg-*K_α*, θ = 0°) for HAIO (74.2 eV) and for the composite (Al: 72.1 eV, Al₂O₃: 75.3 eV). Microstructures that are characterized by different chemical compositions and different optical contrasts of the “drawing”, relative to the surrounding matrix, may be generated with an X/Y-table and a CO₂ laser.

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Introduction

Aluminum hydride (AlH₃)^[1,2] and aluminum oxide (Al₂O₃)^[3] are well-characterized, crystalline compounds. In the first case, the compound may be considered a coordination polymer from a molecular point of view. For aluminum oxide, several crystalline and amorphous phases, which are often described as ionic structures, are known.^[4] Well-established compounds of aluminum simultaneously containing hydrogen and oxygen are aluminum hydroxide, [Al(OH)₃, for example: bayerite] and other oxohydroxides such as boehmite, AlO(OH).^[5,6] It is interesting to note that no chemically pure compounds in which hydrogen is directly bound to aluminum have yet been described (for recent developments see the next paragraph). This is even more surprising because aluminum oxohalides with the general formula XAlO (where X = Cl, Br, I) have been well-established for many years and have been structurally

characterized by X-ray diffraction^[7–9] (and for molecular OAlX species in matrix by spectroscopy^[10]).

We were intrigued by the possible existence of HAIO, a compound that may be derived from the oxohalide by formal substitution of the halide by hydride. Instead of using a classical solid-state reaction to synthesize this compound, we chose a molecular route, which seemed to open up the access to metastable compounds or phases. When revising the manuscript in June, we learned that R.J. Wehmschulte and his co-workers have described a powder, obtained in organic solvents, in which HAIO also seems to be present.^[29] This mixed compound, which also contains some organic residues, is synthesized by treating AlH₃*NMe₃ with siloxanes [such as (Me₂SiH)₂O]; the oxygen is thus transposed from silicon to aluminum, while the hydride is partly transferred to silicon, forming Me₂SiH₂. Indeed, some of the spectroscopic data given in this paper^[29] are similar to our results, while others seem to be different. This difference may also be due to the fact that we describe a layer, whereas the alternative route gives a powder.

Results and Discussion

Synthesis and Elemental Composition of HAIO

For the synthesis of HAIO, the gas-phase decomposition of (*t*BuOAlH₂)₂ on metallic substrates heated to 240–250

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°C at low pressures (0.01–0.1 atm) was used.^[11,12] HAIO is formed as a transparent layer on the metallic surface of the sample and may be separated as a glasslike film from the metal surface using cold shock in a liquid-nitrogen bath. Prior to the gas-phase process the whole apparatus is heated, flooded, and pumped several times with nitrogen, argon, or helium, in order to eliminate residual oxygen and water in the apparatus. The most simple way to generate HAIO layers is to direct a constant stream of $(t\text{BuOAlH}_2)_2$ on inductively heated copper, nickel, iron, or platinum substrates in a CVD cold-wall reactor, the principle construction of which was described earlier.^[13] The obtained layers stick well to the metal surfaces if their thickness does not exceed 2–3 μm , and they are stable towards the atmosphere (H_2O , O_2 , H_2S , CO_2) for longer periods of time. The synthetic route used has to be different from the route producing the composite $\text{Al}/\text{Al}_2\text{O}_3$, which requires distinctly higher temperatures (450–500 °C) at the surface of the metallic target, with $(t\text{BuOAlH}_2)_2$ as a precursor^[14,15] (see also next chapters and reference^[16]).

In order to get some insight in the thermal reaction discussed above and in order to analyze the gaseous products of the reaction, we ran the same process with the deuterated molecule $(t\text{BuOAlD}_2)_2$ parallel to $(t\text{BuOAlH}_2)_2$ (where $\text{D} = {}^2\text{H}$). The mass spectra of the two reactions only differ in one mass peak at $m/z = 3$ (HD), which is the signal of highest intensity for the deuterated compound, whereas this peak is completely absent in the mass spectrum when $(t\text{BuOAlH}_2)_2$ is the precursor. A mass fragment $m/z = 4$ is not found in the case of $(t\text{BuOAlD}_2)_2$ (as long as 270 °C is not exceeded), and all signals in both spectra, besides hydrogen, are those of isobutene.

Conducting a constant stream of $(t\text{BuOAlH}_2)_2$ through a quartz tube heated to 300–700 °C and subsequent trapping of the gaseous products in a cold argon matrix leads exclusively to isobutene, in accordance with the mass spectrometry (see Figure 1).

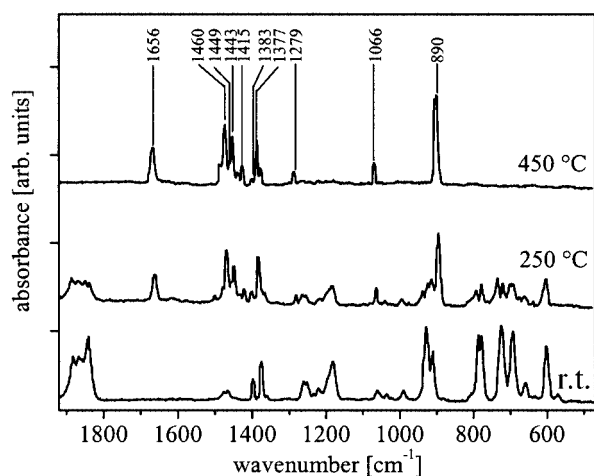
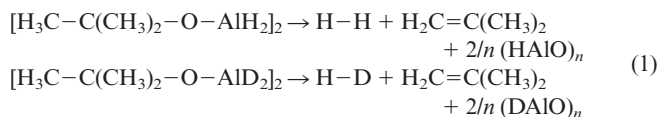


Figure 1. IR spectra of the argon matrix isolated isobutene with identification of the lines (spectrum obtained at 450 °C) and the precursor spectra of $(t\text{Bu}-\text{O}-\text{AlH}_2)_2$ obtained at room temperature (r.t.) and at 250 °C; already at 250 °C the evolution of isobutene, together with residual $(t\text{Bu}-\text{O}-\text{AlH}_2)_2$, is found

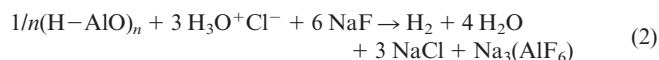
No $(\text{HAIO})_n$ species or any other aluminum compound is trapped in the matrix under these experimental conditions. This observation is a first hint that HAIO must have a high molecular mass and perhaps a complex structure. On the basis of these findings, the reactions may be formulated as in Equation (1).



The splitting off of dihydrogen from $(t\text{BuOAlH}_2)_2$ can be explained by the recombination of a partially negatively charged hydrogen at aluminum with a partially positively charged hydrogen in the *tert*-butyl group, forming isobutene as a complementary molecule (β -elimination). The observed reaction is very similar to the process when $[\text{Mg}\{(\text{OtBu})_2\text{AlH}_2\}_2]$ is transformed to MgAl_2O_4 .^[17]

Whereas the structural and analytical characterization of the gaseous products of Equation (1) is straightforward, the structure and composition of HAIO is not yet clear. From the EDX analysis, the Al to O ratio in HAIO is 0.96(3) to 1.00(3). The carbon content of the film determined by classical elemental analysis is $\text{C} = 0.2(1)\%$, and the hydrogen content has a high standard deviation with a lower threshold value of 0.8% (see also below). The aluminum content, determined by compleximetry, is found to be 60.5(1.0)% near to the 61.4% calculated for HAIO.

In order to make the elemental determination of hydrogen and its relation to the other elements more accurate, we developed a new analytical method. First we deposited a layer of HAIO (around 1.8 mg) on a thin platinum sheet of approximately 30 mg. The layer was then dissolved in a defined volume of 2 N HCl heated to 80 °C. To avoid hydrolysis of the aluminum ion, sodium fluoride was added to the solution. Some aliquots of the solution were taken to determine the former hydroxide content (after HCl addition and by back-titration with NaOH) and others for the determination of the aluminum content by compleximetry. The hydrogen content can be deduced from volumetric measurements of the gas developed from the contact with the acid in a calibrated vessel [see also Equation (2)]. It should be pointed out that freshly prepared samples have to be used and that the HAIO layer should be produced at moderate temperatures (240–250 °C). If higher temperatures are used on the platinum sheet during the deposition process, slightly yellow layers with a significant decrease in the hydrogen content of the layer are obtained.^[18]



From these analyses, the experimental molar ratio of the elements in the layers on platinum are $\text{H}:\text{Al}:\text{O} = 0.95(8):0.95(8):1.0$.

Properties of HAIO

The HAIO layers do not show any reflections when exposed to X-rays. In the infrared spectrum of HAIO (see Figure 2), two signals of different width are found in the 1100–2000 cm^{-1} region: one of these absorption bands at 1925 cm^{-1} is sharp while the other seems to be broad, with a shoulder around 1670 cm^{-1} .

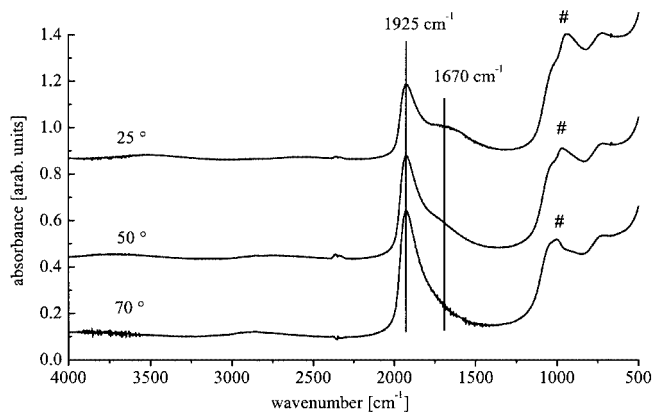


Figure 2. IR spectra of an HAIO layer deposited on a plain copper target in angle-dependent reflection (angles taken between the perpendicular line to the surface and the incoming beam); the signals indicated by # do not belong to the layer and are due to the spectrometer setting

In the deuterated sample DAIO, these absorption bands are found at 1400 and 1223 cm^{-1} , respectively (see Figure 3). The observed isotopic shifts are only understandable for vibrations in which hydrogen takes part, and the values indicate that terminal Al–H (higher wavenumbers) and bridging Al–H \cdots Al entities are both present.^[19,20] From the spectra, shown in Figures 2 and 3, obtained in the reflection mode on films deposited on plain metal substrates, it is evident that there is a correlation between the incident angle of the IR beam and the width and the intensities of the absorptions.

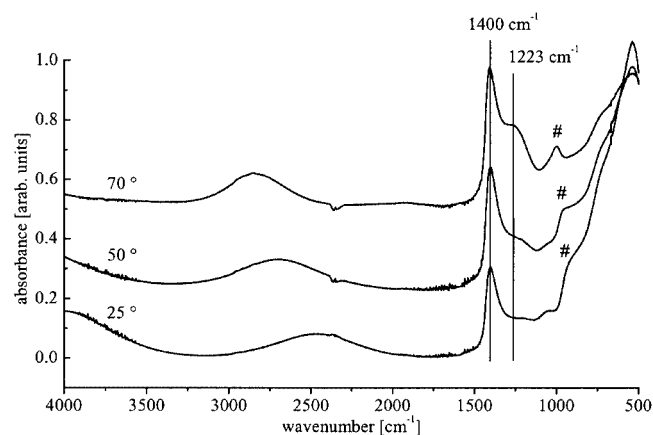


Figure 3. IR spectra of a DAIO layer in angle-dependent reflection with "wrigs"; cf. the comments of Figure 2

Although we have not yet finished our systematic studies, we have noticed that, for example, the relative intensities of the hydrogen-based and oxygen-based vibrations (found in

between 600–900 cm^{-1} with a characteristic shoulder at 730 cm^{-1}) change with the angle of incidence of the IR beam. This change could indicate different orientations between the Al–H and Al–O bonds with respect to the plain surface of the film.^[18]

In the ^1H NMR (MAS) spectrum of the glassy HAIO film separated from the metal target by the shock technique (see above), a broad, structured absorption at approximately 4.0 ppm appears [hydride in $(t\text{BuOAlH}_2)_2$ at $\delta = 4.48$ ppm].^[12] In the ^{27}Al NMR spectrum [see spectrum (e) in Figure 4] absorption peaks are found at $\delta = 6$ (sixfold), 30 (fivefold) and 58 ppm (fourfold coordinated aluminum) indicating an amorphous or complex structure for HAIO.^[21] For comparison, ^{27}Al NMR spectra for amorphous Al_2O_3 {obtained from the thermolysis of $[(t\text{BuO})_2\text{AlH}]_2$ (a)}, for aluminum metal [obtained from the thermolysis of AlH_3 (b)] and for composites Al/ Al_2O_3 [obtained from HAIO at 600 $^\circ\text{C}$ (c) and 450 $^\circ\text{C}$ (d)] are shown in Figure 4. The aluminum metal is nicely characterized through its Knight shift, whereas in the Al–O (Al–H) region (due to more, or less crystallinity and different compositions) the maxima of the peaks are of different intensities. These data, as well as the IR spectrum and the matrix-isolation experiments, indicate that HAIO is not a simple mixing of the distinct phases AlH_3 and Al_2O_3 (compare data in references [2,4,19,20,22]), but could be composed of different structural units.

The XPS analysis of an HAIO film obtained at 250 $^\circ\text{C}$ is consistent with the findings of the spectroscopic methods described so far. In Figure 5, the spectrum (2p-band of aluminum) of an HAIO layer (deposited at 250 $^\circ\text{C}$) is compared to a surface of bulk aluminum that has been partly oxidized (lower part of the figure) and to an HAIO film

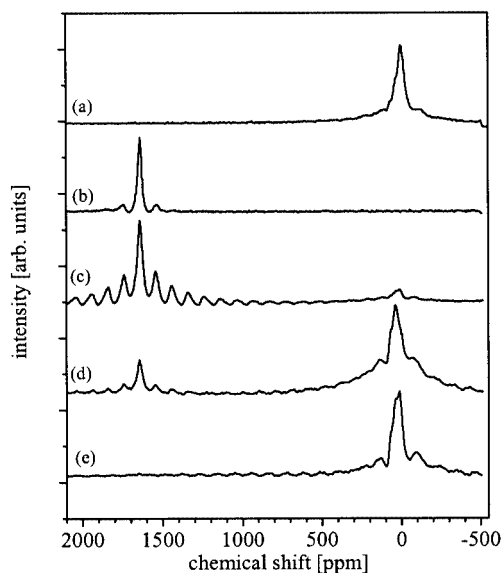


Figure 4. ^{27}Al NMR MAS spectra of (a) amorphous Al_2O_3 obtained from decomposition of $[(t\text{BuO})_2\text{AlH}]_2$, (b) aluminum obtained by decomposition of AlH_3 , (c) solid phase after heating HAIO to 600 $^\circ\text{C}$ under argon, (d) solid phase after heating HAIO to 420 $^\circ\text{C}$ under argon, (e) HAIO obtained from $(t\text{BuOAlH}_2)_2$ at 250 $^\circ\text{C}$

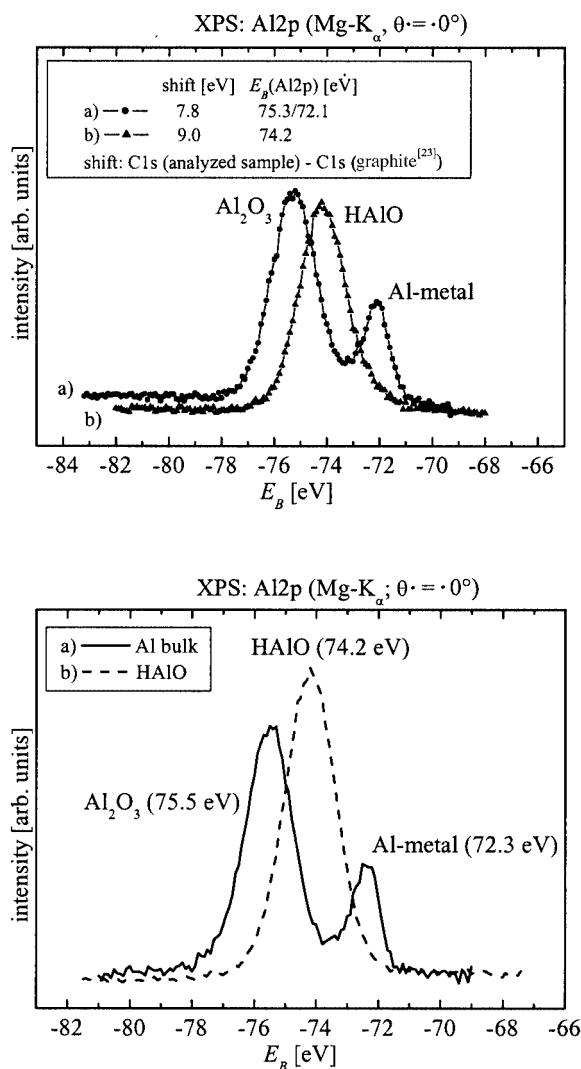


Figure 5. XPS spectra (measured in normal emission); top: the HAIO film obtained at 250 °C from $(t\text{Bu-O-AlH}_2)_2$ (b) and an Al/Al₂O₃-composite, obtained by heating the HAIO film to 550 °C for comparison (a); bottom: the same HAIO film (b) and a partly oxidized aluminum sheet for comparison (a)

that has been heated up to about 600 °C under exclusion of air (see also next paragraph). Compared to Al₂O₃ (Al, 2p-peak found at 75.3 eV), the Al atom in HAIO has a 2p-peak maximum at 74.2 eV, and is shifted towards the energy of the bulk Al metal (Al, 2p-band found at 72.1 eV in the corresponding samples), which is in accordance with the lower electronegativity of hydrogen compared to oxygen.

The bonding of hydrogen to aluminum and the meta-stable property of HAIO can be easily demonstrated by thermolysis of the film.^[16,29] This experiment was repeated with DAIO containing approximately 8% HAIO. In the mass spectrum run simultaneously during decomposition, the evolution of the signal at $m/z = 4$ (D₂) could be followed with increasing temperature and time (see Figure 6).

The hydrogen observed at the beginning may come from the HAIO mixing in the deuterated sample, or may be attributed to residuals on the surfaces of the sample and the apparatus. During the temper process, the color of the layer

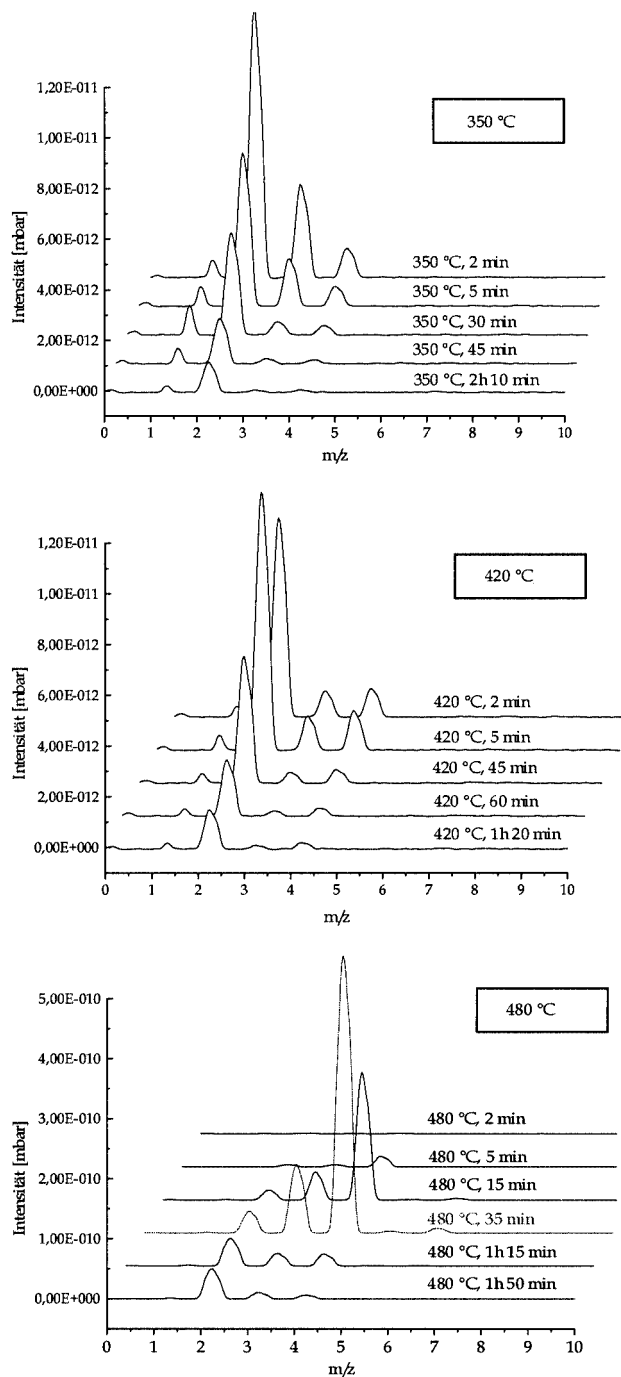


Figure 6. Evolution of H₂ or D₂ from H(D)AlO films (H:D = 8:92) heated at different temperatures, determined by mass spectrometry

changed from transparent to black. The temperature- and time-dependent liberation of hydrogen may also be followed in the infrared spectrum of the film coated on the target, in which the Al–H valence vibration constantly decreases. At the end of the heating process the IR absorption at 1925 cm⁻¹ had completely disappeared (see Figure 7).

At this stage the HAIO film had turned into a biphasic composite film of almost stoichiometric composition, Al/Al₂O₃. Figure 8 contains an X-ray powder diffractogram, which, apart from some non-indexed lines of low intensities

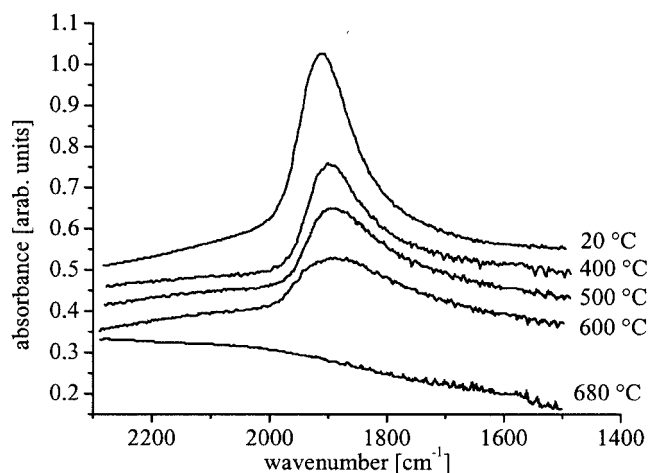
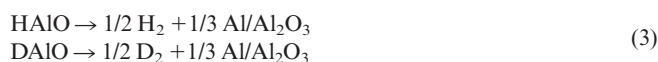


Figure 7. FT-IR spectra of HAIO layers in the 2200–1500 cm^{-1} region heated at different temperatures (heated for 3 minutes before the registration of each spectrum)

at low diffraction angles, consists of two phases: Al and $\gamma\text{-Al}_2\text{O}_3$ (aluminum forms nanoscale crystals; from the reflex profiles in the powder pattern 30–40 nm particles can be deduced;^[24] compare also^[14,15]).

The chemical equations for the tempering are assembled in Equation (3):



The chemical equations in Equation (3) may be interpreted as follows: H (H_2) or D (D_2) is eliminated after breaking of the Al–H or Al–D bonds. The remaining “AlO” (with formal Al^{II}) seems to be unstable at the high processing temperatures and disproportionates to zero- and

three-valent aluminum. Accordingly, the aluminum/oxygen ratio is maintained during the tempering process with an EDX analysis of the composite $\text{Al}:\text{O} = 0.95(9):1.00$ (similar to the precursor HAIO). In the classical CHN analysis, the carbon content remains 0.2(1)%, while no hydrogen can be detected.

Instead of transforming the whole surface by heating, locally defined regions may be transformed using a 12.5-W CO_2 laser together with a motor driven x/y -table. By this technique various structures may be produced on the surface of the film.

In Figure 9, a 600 μm large letter, with a line width of approximately 70 μm , which is dark gray and is composed of Al/ Al_2O_3 composite, is seen. The area around the letter is still made up of metastable HAIO, whereas in the infrared spectrum taken within the letter, no vibrations due to Al–H can be detected.

Conclusions

The formation of HAIO (DAIO) films by thermolysis of $(t\text{BuOAlH}_2)_2$ on hot metallic substrates has been shown to proceed via β -elimination of dihydrogen and isobutene. Although the HAIO layers are almost stoichiometric in hydrogen, aluminum and oxygen, their structure is not yet clear. Like in other amorphous glasses, there may be different structure entities present, which, according to NMR spectroscopy, seem to have four, five, and sixfold coordination sites around aluminum. HAIO films are metastable and lose hydrogen when heated. At a certain point disproportionation of intermediate Al(II) is observed, forming aluminum and aluminum oxide. From the infrared spectra, the presence of Al–H(D) bonding is beyond doubt; even under high reflection angles we have not yet been able to detect hydroxide on the surface of the films by infrared

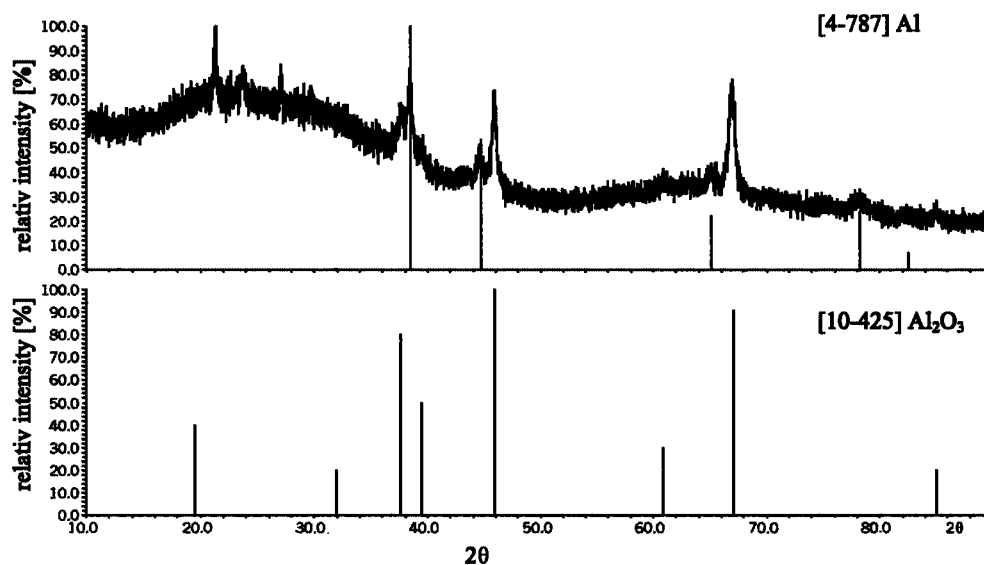


Figure 8. X-ray powder pattern of an HAIO layer on steel tempered at 510 $^{\circ}\text{C}$; the reflections at lower 2θ values seem to come from reactions of the iron surface, as they are almost absent on other metal surfaces; the reflections at higher angles can be indexed with Al^[27] and $\gamma\text{-Al}_2\text{O}_3$ ^[28]

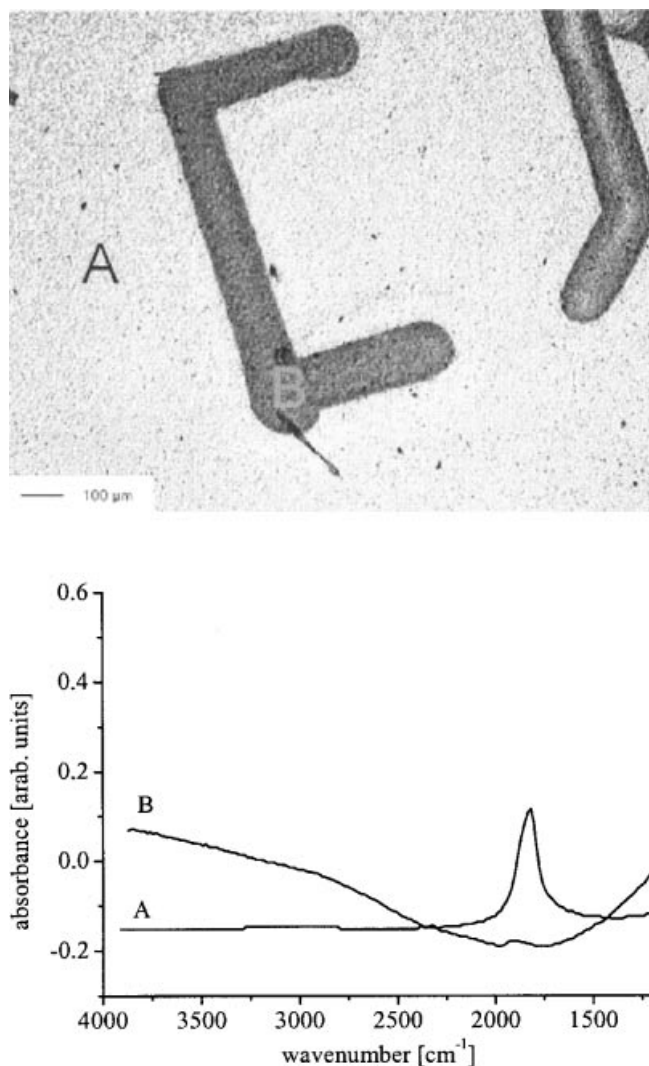


Figure 9. Light microscopy picture of a 3 μm thick HAIO layer, on which an Al/Al₂O₃-microstructure has been produced with a CO₂ laser (the sample was moved with respect to the laser beam with a velocity of 200 μm/s); the transparent (A) and the dark (B) spots show different absorptions in the Al–H region of the IR spectrum (reflection mode)

spectroscopy, although we cannot exclude it completely. More sophisticated measurements on the structure of HAIO are on the way.

Experimental Section

General Remarks: The precursor compound (*t*BuOAlH₂)₂ is synthesized following the routes described before^[11,12] under dry N₂ using standard Schlenk techniques. The deuterated sample (*t*BuOAlD₂)₂ was obtained from LiAlD₄ instead of LiAlH₄. Solvents were dried by refluxing with appropriate drying agents and were distilled before being used. CVD was carried out in a cold-wall reactor as described in an earlier publication^[13]. The CVD reactor consists of a cylindrical reaction tube in which the metal substrate is situated on a glass support. The substrate is heated inductively at temperatures ranging from 250–500 °C. The temperature of the substrate is measured by a thermocouple and is connected to the high frequency source to monitor the temperature.

The quadrupole mass spectrometer is linked to the system and enables monitoring of the reaction gases.

Physical Measurements: The C, H analyses were carried out using a CHN analyzer from LECOTM Corporation, St. Joseph, MI., U.S.A. IR spectra of the produced solid film were obtained using a Bio-Rad FTS 165 with a mirror unit for direct reflection. ²⁷Al solid-state MAS NMR spectra were measured on a Bruker 200 MHz-MSL 200 with magic angle spinning (MAS). The powder X-ray diffraction measurements were performed in a glass capillary on a STOE diffractometer using Cu-K_α and a linear PSD detector. The XRD patterns of layer material were compared with literature values.^[27,28] Electron microscopy and energy dispersive X-ray (EDX) analyses were performed on a scanning electron microscope CAMSCAN S4 with Si(Li)-semiconductor detectors and with thin windows (Cameca and Noran). The mass spectra of the pyrolysis gases were recorded on a quadrupole mass spectrometer QMS 200 (Balzer). The cryostat used for the matrix isolation of the pyrolysis gases and the deposition conditions are described in an earlier publication.^[25,26] The IR spectra of the pyrolysis products were obtained with a Bruker IFS 113 v FT-IR spectrometer. The XPS spectra were recorded on a VG ESCA MKII spectrometer with a Mg-K_α-source (*E*_{kin} = 1253.6 eV, *E*_{pass} = 10 eV, Δ*E* ≈ 0.8 eV). The HAIO film was heated successively up to 600 °C on a micro-heating table TS 1400 (Linkham) under N₂ atmosphere. The tempering was monitored by IR spectrometry. Laser-structuring of the HAIO film was achieved by a CO₂ laser (LC-25, DEOS) of 25 W. In the optical pathway between laser and film surface, layer gold-coated, optical lenses (*f* = 2.5 mm) were used for focussing, while the target was positioned by use of a micro-driven mechanical X/Y-table.

Preparation of Compounds

CVD Process of (*t*BuOAlH₂)₂ [(*t*BuOAlD₂)₂] and Synthesis of HAIO (DAIO): The thermal decomposition of the alkoxide precursor (*t*BuOAlH₂)₂ [(*t*BuOAlD₂)₂] was performed in a CVD apparatus. The experimental setup consists of a high vacuum line with Ar as the inert gas and a metal (steel, copper, nickel, platinum) support, which is inductively heated at 250 °C. The volatile precursor is transported to the substrate at pressures around 6.0 × 10^{−2} mbar. The volatile decomposition products (hydrogen, isobutene) were analyzed by online mass spectrometry. The precursor deposits on the substrate as a transparent HAIO layer. The CHN analysis of HAIO (43.989 g/Mol) gave a mean C value of 0.2(1), a range for H of 0.8 to 2.1% (calculated: 2.31%) and a value for N of 0(0.1)%. EDX analysis agrees with an Al/O ratio of 0.96(3):1.00(3). The titrimetric analysis of Al content (with titriplex as complexing ligand) gave a value of 60.5 (1.0) wt% (calculated Al in HAIO: 61.4 wt%). In order to determine the content of aluminum with respect to hydroxide in the same sample (after hydrolysis of HAIO, see also Equation 2), we used a known concentration of aqueous HCl and a standard solution of NaOH for back-titration. In a typical experiment, a layer of HAIO (1.212 mg, 0.0276 mMol) deposited on a platinum sheet gave 0.028(4) mMol aluminum and 0.087(4) mMol of hydroxide, consistent with a H:Al:O ratio of 1.05:1.01:1.05. The volumetric determination of the hydrogen evolved during hydrolysis in a calibrated tube (under standard conditions), gave typically 95% of the assumed hydrogen content. The reflectance IR spectra of the HAIO thin layer show an absorption at 1925 cm^{−1} (valence vibration for terminal Al–H groups), a shoulder at 1670 cm^{−1} for bridging Al–H···Al groups, and a broad band between 900 and 600 cm^{−1} with a typical shoulder at 730 cm^{−1} (Al–O groups). The ¹H-MAS solid NMR spectrum of HAIO shows a wide, structured absorption with a maximum at 4.0 ppm. The ²⁷Al-MAS solid NMR spectrum shows peaks at 6, 30 and 58 ppm. The binding

energy of the 2p-signal of aluminum in HAIO was found at 74.2 eV in the XPS spectrum.

Synthesis of Al/Al₂O₃ by Annealing of HAIO: The HAIO sample was tempered on a micro-heating table under N₂ atmosphere or was heated inductively in the CVD reactor under vacuum conditions (1×10^{-2} mbar). The annealing of the HAIO at 500 °C for one hour transforms the transparent layer into a black Al/Al₂O₃ composite. The XRD pattern of the Al/Al₂O₃ is shown in Figure 8. EDX analysis agrees with an Al/O ratio of 0.95(9):1.00. The CHN analysis of the composite gave a mean C value of 0.2(1)%, and almost no H and N. In the IR spectrum a broad absorption is found between 900 cm⁻¹ and 600 cm⁻¹. During the temper process of HAIO (DAIO) the hydrogen elimination was detected online by a quadrupole mass spectrometer linked to the CVD apparatus (see also Figure 6). The XPS analysis shows the binding energies of two 2p-signals of aluminum: at 75.3 eV for Al₂O₃ and at 72.1 eV for Al, in agreement with the literature.^[23] The peaks were shifted towards the Cls peak ($E_B = 284.3$ eV).

Synthesis of Al/Al₂O₃ by CO₂ Laser Treatment of HAIO: The HAIO sample was laser-treated by a CO₂ laser (12.5 W) in air. The transparent HAIO layer changes to display black Al/Al₂O₃ composite patterns. In the IR spectra (microscopic setup) of the Al/Al₂O₃ patterns, the Al–H valence bands at 1925 cm⁻¹ and 1670 cm⁻¹ disappear, whereas the broad absorption between 900 cm⁻¹ and 600 cm⁻¹ is maintained.

Acknowledgments

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