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DAMAGE OF OXIDE LAYERS ON AN AL-ALLOY BY ELECTRON BOMBARDMENT

by

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Abstract:

Electron and photon stimulated neutral gas desorption from technical metal surfaces after heat treatment in an UHV environment is in general determined by chemical reactions at the oxide layer which is always present on these materials rather than by molecules simply physisorbed on the surface.

The desorption rate of the neutral gases H_2 , CH_4 , H_2O , CO and CO_2 from the surface of an Al-alloy and its decrease during continued 300 eV electron bombardment has been studied. In parallel the changing surface composition was measured by Auger electron and X-ray photoelectron spectroscopy. During continuous electron bombardment the original aluminium hydroxide on the surface is reduced and carbides are formed. These processes are frequently called radiation damage.

In addition the readsorption and the recontamination of a cleaned Al-alloy surface by the above mentioned gases during exposure to atmosphere was measured. Chemical reactions between the surface and water vapour were shown to play an important role in the recontamination of the surface.

1. Introduction

Electrons and photons can cause the desorption of atoms and molecules from solid surfaces. This desorption becomes relevant for a number of present technologies like for example in electron and positron storage rings where the electron and photon stimulated desorption (ESD and PSD) of the neutral gases H_2 , CH_4 , CO and CO_2 plays an important role in determining the beam lifetime. The origin of these gases is mainly from the oxide layer, which is omnipresent on metals and alloys commonly used in vacuum technology [1]. It is now well established, that electron and photon beams are reducing agents for oxides and cause decomposition of oxides via processes like 'Coulombic explosion' [2] and 'Franck - Condon excitation' [3]. The overall effect is frequently called radiation damage.

Our attention is directed towards the quantification of this radiation damage of technical surfaces, relevant in vacuum technology. Samples of an extruded aluminium alloy profile were chosen and the radiation damage during continuous electron bombardment is characterized in terms of the:

- integrated desorbable gas load,
- changing of chemical states monitored by Auger electron spectroscopy,
- variation of the electron induced molecular gas desorption with time and electron dose.

Recontamination experiments where a 'clean' surface is exposed to water and other contaminants provide further information about the processes determining the desorption.

2. Aparatus and experimental Details

The Auger electron spectroscopy (AES) system and the desorption measuring equipment using electrons have already been described in a previous publication [4], in what the AES system operates with an electron flux of $1.7 \cdot 10^{17} \text{ e}^-/\text{s cm}^2$ and at energy of 2 keV. For the ESD measurements, the electrons were accelerated from a hot tungsten filament towards the biased (+ 300 V) sample. The electron flux was typically about $4 \cdot 10^{13} \text{ e}^-/\text{s cm}^2$, but in case of very low desorption yield it was increased to $3 \cdot 10^{15} \text{ e}^-/\text{s cm}^2$ for short periods.

The molecular desorption yield is derived from the specific pressure rise and a known pumping speed via a calibrated conductance. But the system walls provide an additional unknown pumping speed, which is most important for water vapour and, hence, cause large uncertainties in the measurement of the desorption of H_2O . For this reason it will not be possible in the following to give the variation of the water desorption with time.

Prior to each recontamination experiment the samples were cleaned by a DC argon glow discharge (AGD). After exposing the sample to a total dose of about $3 \cdot 10^{18} \text{ Ar}^+/\text{cm}^2$ (the sample was biased negativ (- 380 V) with respect to the surrounding vacuum chamber) the sample surface was almost oxygen and carbon free, see fig.2d.

The material studied was the aluminium alloy ISO AlMgSi (Mg 0.5%, Si 0.5%, Al – balance) cut from an extruded vacuum chamber profile. The geometrical area, exposed to the electron bombardment, was 15 cm^2 . Surface roughness measurements with a corrugmeter and scanning electron microscopy suggest that the real microscopic surface area, considering uneveness on the scale between 1 and $100 \mu\text{m}$, is at least twice as big as the geometrical surface. But to avoid misunderstanding, all values reported here are referred to the geometrical surface area.

3. Oxide Decomposition

1. Initial Oxide Layer

After the chemical cleaning of the sample [5], etching with NaOH and HNO₃ and rinsing in demineralized water as last steps, the aluminium alloy is covered with hydroxide Al(OH)₃ layer, presumably Gibbsite [6]. X-ray photoelectron spectroscopy (XPS) confirms an aluminium–oxygen ratio of 1:2.7. Furthermore carbon (15 %), MgO (0.7 %) and traces of the cleaning solutions are found on the surface. The carbon on the surface is very unstable when bombarding with the AES electron beam, already for a electron dose $d \approx 2 \cdot 10^{19} \text{ e}^-/\text{cm}^2$, which corresponds to a measuring time of 100s, 50% of the carbon is removed. The thickness of the hydroxide layer, which was determined both by XPS and AES measurements, is about $35 \text{ \AA}$.

Baking the aluminium in an UHV environment for 15h at 150 °C (mounted on a heated sample-holder in the XPS system, and together with the whole vacuum system for the AES) changes the surface composition. The Al–O ratio is still about the same (Al:O = 1:2.6) but the carbon content increases dramatically. XPS indicates an average carbon content of 44 atomic % in the oxide layer and AES a carbon content of 73 atomic % in the near surface region after the bakeout. This carbon peak is now stable during the Auger analysis.

2. Integrated Gas Load

During the electron bombardment ($E_e = 300 \text{ eV}$) the hydroxide layer on aluminium decomposes. The products of this decomposition, hydrogen and oxygen, together with the always present carbon, form all possible compounds, but mainly the molecules H₂, CH₄, H₂O, CO and CO₂.

The desorption of the neutral gas molecules was measured during the electron stimulated desorption experiment, as shown in fig.1. The total quantity of desorbed gas and the corresponding number of desorbed hydrogen, oxygen and carbon atoms relative to the geometrical surface, after exposure of the sample to a total electron dose d of $d = 3.0 \cdot 10^{20} \text{ e}^-/\text{cm}^2$, are listed in table 1.

The theoretical hydrogen content of a $35 \text{ \AA}$ thick Al(OH)₃ – layer on aluminium, when assuming a complete decomposition of the hydroxide, is about a factor 4.0 smaller than the quantity of hydrogen desorbed. Since this factor is close to the surface roughness factor suggested by the scanning electron

microscopy of the aluminium sample and in the range of the surface roughness factor $R = 2.6 - 14$ for stainless steel determined by Xenon adsorption [8], the discrepancy between measured and calculated data is mainly ascribed to the surface roughness of the sample. Hence, the real surface area of our extruded sample exceeds the geometrical surface area by a roughness factor of $R = 4.0$.

	H ₂	CH ₄	H ₂ O	CO	CO ₂
Integrated gas load [molecules/cm ²]	7.5 10 ¹⁶ (5.6 10 ¹⁶ *)	6.9 10 ¹⁴	1.5 10 ¹⁵	7.2 10 ¹⁵	3.8 10 ¹⁵
	H _{oxide} *	H _{bulk}	O	C	
Integrated gas load [atoms/cm ²]	1.1 10 ¹⁷	0.5 10 ¹⁷	1.5 10 ¹⁶	1.2 10 ¹⁶	
Calculated gas content [atoms/cm ²]	1.1 10 ¹⁷	2.0 10 ¹⁷	1.1 10 ¹⁷	1.0 10 ¹⁷	

* Hydrogen originating in the oxide layer, see section 4

Table 1: Integrated gas load after a beam dose of $3 \cdot 10^{20} \text{ e}^-/\text{cm}^2$ and the calculated number of atoms in a 5 mm thick aluminium sample (including a surface roughness factor 4.0), covered by a 35 Å thick Al(OH)₃ layer.

The bakeout at 150 °C releases the physisorbed water and other physisorbed gases from the sample surface, but hardly any Al(OH)₃ is transformed to Al(OH) [7] during the relatively short bakeout time. The electron stimulated decomposition of the hydroxide is completed at relatively low electron dose. The kinetic data, see section 4, suggest a complete release of the hydrogen out of the hydroxide for a dose $\approx 2 \cdot 10^{19} \text{ e}^-/\text{cm}^2$. This layer is now more stable. Up to a dose of $3 \cdot 10^{20} \text{ e}^-/\text{cm}^2$ only 10% of the total carbon and oxygen content of the layer on aluminium are desorbed. For high electron dose $> 3 \cdot 10^{21} \text{ e}^-/\text{cm}^2$, a reduction of oxidized aluminium to pure aluminium metal is reported by Van Oostrom [9]. It is noted finally that pure metals are not, in general, subject to radiation damage during electron bombardment [10] for the low e^- energies considered here.

According to these considerations the overall desorbable gas load is the gas content of the omnipresent hydroxide layer on aluminium together with the hydrogen content of the aluminium bulk material, as listed in table 1.

Fig.1: Neutral molecular gas desorption yield η for H_2 , CH_4 , CO , CO_2 as a function of the accumulated electron dose ($E_{electron} = 300 \text{ eV}$) for aluminium.

3. Auger Analysis

After exposing the sample to electron doses of $4 \cdot 10^{18}$, $1.5 \cdot 10^{20}$ and $3 \cdot 10^{20} \text{ e}^-/\text{cm}^2$ ($E_e = 300 \text{ eV}$) the surface composition was analysed by AES, see fig.2 a,b,c. The electron beam density of our Auger analysis system made analysis at a lower electron dose impossible.

The Auger spectrum is influenced by the preceding 300 eV electron bombardment. The most significant low energy Al peaks at 38 and 55 eV shift to a single peak at 61 eV. In parallel the carbon peak increases despite the desorption of carbon in the form of CO , CO_2 and CH_4 . This increase cannot be attributed to a readsorption of carbon out of the gas phase, because the electron bombardment of a AGD cleaned sample does not show this effect.

It appears that carbon builds up a superficial layer on the surface during electron bombardment. The shape of the carbon peak suggests that the carbon layer on the surface is in the form of graphite. The two low energy Al Auger peaks are found when water is adsorbed on aluminium and are assigned to Al-OH bondings [11]. The chemical composition of the aluminium compound is changed during electron bombardment, but neither Al_2O_3 , with an Al-Auger peak at 51 eV [12,13], nor pure Al metal, Auger peak at 68 eV [13], are formed in a measurable amount. The partial carburization of alu-

minium with electron bombardment is not excluded. It is of interest to note that during previous measurements with a low carbon coverage on aluminium the shape of the Auger carbon peak was found to be similar to the carbon peak of carburized nickel [14].

Fig.2: Auger electron spectra for an aluminium sample which was exposed to

- a) a electron dose $d \approx 4 \cdot 10^{18} \text{ e}^-/\text{cm}^2$,
- b) $d = 1.5 \cdot 10^{20} \text{ e}^-/\text{cm}^2$,
- c) $d = 3.0 \cdot 10^{20} \text{ e}^-/\text{cm}^2$,
- d) argon glow discharge cleaning (AGD),
- e) AGD + recontaminated by 'dry' N_2
- f) AGD + recontaminated by N_2 (purity 4.5)

4. Variation of the Electron Stimulated Desorption with Time and Electron Dose

As said previously it is mainly the neutral gases H_2 , CH_4 , H_2O , CO and CO_2 which are desorbed by 300 eV electrons. The initial molecular desorption yield η expressed in desorbed molecules per incident electron and the variation of η versus the electron dose during continuous electron bombardment are shown in table 2 and fig.1.

The molecular desorption yield for the various gases depends, among other things, on the probability to form the gas molecule during concurrent chemical reactions e.g. the concurrent formation of CO and CO_2 out of carbon and oxygen. This probability can shift during the experiment. Only the formation of H_2 is so dominant, that it is possible to analyse the time and electron dose dependence of the molecular desorption yield η in terms of a simple transport model. This model was introduced in previous publications as a 'Diffusion model' [1,15,16]. Here, the main predictions of the model are re-

viewed, because they allow one to distinguish between hydrogen originating in the bulk and in the oxide. In analysing η as a function of the electron dose it is convenient to identify (as indicated in fig.1) the four different phases :

A: a starting period with low cleaning rate ($\eta \approx \text{constant}$)

B: a certain time with a constant cleaning rate due to the hydrogen diffusion out of the oxide layer
($\eta \propto d^{-1/2}$)

C: an enhanced cleaning rate due to the depletion of the oxide layer

D: constant cleaning rate, again with $\eta \propto d^{-1/2}$ due to the hydrogen contribution from the aluminium bulk material.

The measured values for the hydrogen desorption in fig. 1, are fitted according the diffusion model using the above mentioned data for the initial hydrogen concentration in the aluminium hydroxide and for the oxide thickness. In addition the hydrogen concentration at the aluminium-aluminiumoxide interface $c = 2 \cdot 10^{-1} \text{ cm}^3(\text{STP})/\text{cm}^3$, and the diffusion constant D of hydrogen in the hydroxide $D = 3 \cdot 10^{-18} \text{ cm}^2/\text{s}$ ($T = 35^\circ\text{C}$) [1] are assumed. (The assumed value for the hydrogen concentration at the interface aluminium - oxide is somewhat higher than the average hydrogen concentration in the aluminium bulk material $c = 2 \cdot 10^{-2} \text{ cm}^3(\text{STP})/\text{cm}^3$ [17]). Deviations from the measured desorption behaviour for the 'enhanced cleaning phase' might be caused by variations in the oxide layer thickness and the electron intensity. Small, local differences in the oxide thickness and radiation intensity may extend the 'enhanced cleaning' phase over a broad electron dose range e.g. a oxide thickness which varies between 35 and 60 Å would fully explain the extended 'enhanced cleaning' phase.

The time dependence of the desorption of oxygen in the form of CO and CO₂ is similar to the hydrogen desorption. But for a high electron dose a different mechanism such as the lowered decomposition rate, because of the more stable oxide and the fact that the aluminium bulk cannot be a source for oxygen, cause a different cleaning rate. For very high electron doses it is for all gases doubtful whether the diffusion model is applicable because of the changing oxide properties.

4. Recontamination

Two series of recontamination experiments were made with aluminium samples cleaned by AGD preceding each experiment. During the first series the sample was exposed successively to about $4 \cdot 10^4$ L ($1 \text{ L} = 1.33 \cdot 10^{-6} \text{ mbar s}$) H_2 and CO. The hydrogen gas desorption yield η_{H_2} was almost unaffected by this treatment and η_{CO} increased from $5 \cdot 10^{-7}$ to $1.3 \cdot 10^{-5} \text{ mol/electron}$. This recontamination is small compared to the recontamination of the surface by exposures to a pressure of one atmosphere to:

- N_2 (H_2O contamination frozen out in a liquid nitrogen trap, $\text{O}_2 \approx 10 \text{ ppm}$)
- N_2 ($\text{H}_2\text{O} \approx 10 \text{ ppm}$, $\text{O}_2 \approx 10 \text{ ppm}$)
- ambient air

These experiments indicate a dominant influence of the water on the molecular gas desorption yield (as found also for stainless steel [18]), see table 2. Depending on the presence of some water contamination and independent of the oxygen impurity of the inert nitrogen gas the aluminium surface is either hardly oxidized or almost as strongly oxidized as by exposure to air. The Auger spectrum see fig.2e , shows a very thin oxide layer after the first recontamination with 'dry' N_2 . This oxide layer is still transparent for the low energy aluminium metal Auger electrons. By contrast, after the recontamination experiments with 'wet' nitrogen the surface was covered with a thick oxide layer (fig.2f). The electron induced molecular desorption yields were comparable to that from the original sample surface after the recontamination both with the 'wet' N_2 and with air.

The desorption of the gases CO, CO_2 and CH_4 is largely independent of the carbon coverage on the surface measured by AES. At carbon coverage at the detection limit (0.5%) of the AES system the desorption yields are still as high as measured with more than 70% of carbon on the surface. This again supports the conception that oxide decomposition is the determining step of the desorption. An interesting observation is that a low carbon coverage (about several atomic %) is removed by the recontamination with 'wet' N_2 . Carburized aluminium is hydrolysed when exposed to water [19] and, hence, the carbon vanishes when oxidizing the aluminium.

Treatment	η [mol/electron]				
	H ₂	CH ₄	H ₂ O	CO	CO ₂
unbaked	1.1	3.0 10 ⁻²	3.0 10 ⁻¹	1.0 10 ⁻¹	1.2 10 ⁻¹
baked	5.7 10 ⁻¹	1.2 10 ⁻³	5.5 10 ⁻³	5.8 10 ⁻²	8.3 10 ⁻²
after AGD	2.0 10 ⁻⁵	2.2 10 ⁻⁷	< 5.0 10 ⁻⁷	4.2 10 ⁻⁷	< 2.0 10 ⁻⁷
N ₂ (dry)	7.2 10 ⁻³	3.6 10 ⁻⁵	1.2 10 ⁻⁵	1.1 10 ⁻⁴	2.5 10 ⁻⁶
N ₂ (10 ppm H ₂ O)	6.0 10 ⁻²	4.6 10 ⁻⁴	2.8 10 ⁻⁵	1.9 10 ⁻³	6.1 10 ⁻⁴
air	6.2 10 ⁻²	4.0 10 ⁻⁴	4.5 10 ⁻⁴	3.5 10 ⁻³	4.5 10 ⁻³

Table 2: Initial molecular gas desorption yield η in molecules per electron for aluminium before and after bakeout, after AGD and after exposure for 1 h to 1 bar N₂(dry), N₂ (purity 4.5) and air, whereby each reexposure was preceded by an AGD cleaning of the sample.

5. Summary

The combination of the measurement of the desorption of the neutral gas molecules H₂, CH₄, H₂O, CO and CO₂, stimulated by electrons, and AES surface analysis leads to a better understanding of the desorption process from a technical aluminium surface. In a first step the Al(OH)₃ layer on aluminium decomposes whereby the total hydrogen and about 10% of the oxygen and contaminating carbon content of the layer are desorbed. In parallel carbon, from the contamination in the hydroxide layer, builds up a superficial graphite layer. Later electron bombardment releases hydrogen from the aluminium bulk material and reduces the oxide layer with aluminium metal as the final product. Several observations by AES support the conception that aluminium is partially carburized by the electron bombardment.

This work is confined to electron induced radiation damage because of the accessible experimental facility, but most of the remarks apply to photons as well. The step from electrons to photons might be explained on the basis of the secondary electron production [1].

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