THE TEMPERATURE DEPENDENCE OF THE ELECTRON AND
ION INDUCED GAS DESORPTION COEFFICIENTS
OF SOME TECHNOLOGICAL MATERIALS

by

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1. INTRODUCTION

In vacuum systems of electron and proton storage rings and prototype fusion reactors where the inside walls are subjected to energetic electron\textsuperscript{1} and/or ion bombardment\textsuperscript{2,3}, it is desirable that the surfaces be free of all desorbable gas. To reach base pressures in the \(10^{-11}\) to \(10^{-12}\) torr range, such vacuum systems are normally baked at \(200^\circ\text{C}\) or \(300^\circ\text{C}\) to reduce the thermal outgassing from the walls. However, even after 24 hours at \(300^\circ\text{C}\) some tightly bound surface gas may remain\textsuperscript{4,5} and subsequently desorb under energetic particle bombardment and impair the functioning of the machine\textsuperscript{2}. By the choice of vacuum chamber materials with suitable mechanical properties at elevated temperatures, and by appropriate chamber design, the bakeout temperature may be increased sufficiently to deplete the surface concentration of tightly bound gas. Such materials include 316 L + N stainless steel, Inconel 600, Inconel 718 and titanium (Ti Al 6 V4). Because of its use as an absorber of synchrotron radiation in electron and positron storage rings OFHC copper was also investigated. In addition, an aluminium alloy (5086) was also studied because of its better transparency to secondary particles compared to these other materials and hence its potential usefulness as an intersection region vacuum chamber material. To investigate the surface properties of these materials after heating to high temperature in vacuo the electron and ion induced desorption coefficients (\(\eta\)), i.e. the number of gas molecules desorbed by each incident electron or ion, were measured up to \(600^\circ\text{C}\). The Al alloy, because of its limited high temperature mechanical properties, was only heated to \(300^\circ\text{C}\). The measured desorption coefficients were correlated with the temperature dependence of surface composition as determined by Auger electron spectroscopy.

2. APPARATUS

The Auger electron spectroscopy system and the desorption measuring equipment using electrons and \(\text{k}^+\) ions have already been described in previous publications\textsuperscript{6,7}. The desorption apparatus had, however, the addition of a sample holder which could be heated to \(600^\circ\text{C}\). The samples (6 \(\times\) 7 cm) were clamped on to this holder and their temperature measured with a chromel-alumel thermocouple spot welded to the surface subjected to bombardment. Heating to above \(600^\circ\text{C}\) tended to cause sublimation from the samples of base material which condensed on the system walls providing an additional unknown pumping speed in the system and hence large uncertainties in the measurement of \(\eta\).

The samples were all vapour degreased in perchlorethylene vapour, ultrasonically cleaned in alkaline detergent, rinsed in demineralized water and finally dried in a hot air oven at \(150^\circ\text{C}\).
3. TEMPERATURE DEPENDENCE OF THE DESORPTION COEFFICIENTS

A sample was cleaned and installed in the measuring equipment. After sufficient pumping time to reach a pressure \( p = 1 \times 10^{-8} \) torr, usually about 2 days, a measurement of \( n \) was made. The complete system was then baked at 150\(^\circ\)C, 200\(^\circ\)C or 300\(^\circ\)C for 24 hours to give a good base pressure \( p = 2 \times 10^{-10} \) torr and the desorption coefficients measured again. Sample temperatures higher than these bakeout temperatures were obtained by heating only the sample for 24 hours in this now baked system, then, after cooling, again measuring the desorption coefficients. The procedure was repeated in steps of 100\(^\circ\)C up to 600\(^\circ\)C for the OFHC copper, titanium, Inconel 600 and the Inconel 718. For the aluminium alloy the measurements were carried out up to only 300\(^\circ\)C in 50\(^\circ\)C steps from the system bakeout temperature of 150\(^\circ\)C. After the system with the stainless steel sample installed was baked at 150\(^\circ\)C, the sample was then heated to 300\(^\circ\)C in 50\(^\circ\)C steps and from 300\(^\circ\)C to 600\(^\circ\)C in 100\(^\circ\)C steps.

Only \( \text{H}_2 \), \( \text{CH}_4 \), CO and \( \text{CO}_2 \) were seen to be desorbed by electrons or ions from the six metals studied, i.e. apart from the \( \text{H}_2 \) the desorbed species are C based.

In Figures 1, 2, 3, 4, 5 and 6 are shown the temperature dependence of the electron and ion induced desorption coefficients for 316 L + N stainless steel, titanium alloy, Inconel 600, Inconel 718, OFHC copper and aluminium alloy respectively at a bombardment energy of 1400 eV; (this energy corresponding to the energy of residual gas ions produced by a typical ISR proton beam. The electron induced desorption coefficients for the aluminium alloy were measured at 600 eV, this being the energy at which in aluminium they are a maximum \(^8\)).

It is seen that on a logarithmic scale both desorption coefficients decrease almost linearly with increasing bakeout temperature and that the electron induced desorption coefficients decrease about ten times faster.

In general, before bakeout the electron induced desorption coefficients are about an order of magnitude lower than the ion induced desorption coefficients. After heating to 600\(^\circ\)C for 24 hours the difference increases to about two orders of magnitude.

On all six metals the \( K^+ \) ion induced desorption coefficients at 1400 eV for \( \text{H}_2 \) and CO (i.e. \( n_{\text{H}_2} \) and \( n_{\text{CO}} \)) are largest and of the same order of magnitude. They are followed by \( \text{CO}_2 \) and \( \text{CH}_4 \), both these being about an order of magnitude lower.
For the electron induced desorption the order is somewhat different. The largest is $\eta_{\text{H}_2}$ followed by $\eta_{\text{CO}_2}$ and $\eta_{\text{CO}}$ and finally $\eta_{\text{CH}_4}$. As can be seen from the figures this order is not strictly maintained over the temperature range of interest but is in general true. The different temperature dependence and different desorption efficiencies for the electrons and ions are explicable in terms of the different desorption mechanisms. Under ion bombardment the desorption takes place by momentum transfer between the incident ion and the adsorbed gas molecule (possibly via the substrate) whereas in electron induced desorption the adsorbed atom is first excited to an antibonding state by the incident electron which interacts with the binding electrons.

At 1400 eV before bakeout all six metals gave, for ion bombardment, $\eta_{\text{H}_2}$ and $\eta_{\text{CO}}$ values of the order of 10 or 20 mol. ion$^{-1}$, $\eta_{\text{CO}_2}$ values between 2 and 7 mol. ion$^{-1}$ and $\eta_{\text{CH}_4}$ values between 0.5 and 1 mol. ion$^{-1}$. Heating to 600°C reduced $\eta_{\text{H}_2}$ and $\eta_{\text{CO}}$ to below 1 for all metals except OFHC copper where they remained between 1.5 and 2.5 mol. ion$^{-1}$. For $\eta_{\text{CO}_2}$ and $\eta_{\text{CH}_4}$ these coefficients were in the low $10^{-1}$ to $10^{-2}$ mol. ion$^{-1}$ range.

Before bakeout for electron bombardment $\eta_{\text{H}_2}$ values between 6 and 0.4 mol. electron$^{-1}$ were measured, $\eta_{\text{CO}}$ and $\eta_{\text{CO}_2}$ values between 2 and 0.25 mol. electron$^{-1}$ and $\eta_{\text{CH}_4}$ values ranging from 0.55 mol. electron$^{-1}$ for Al to $2 \times 10^{-2}$ mol. electron$^{-1}$ for stainless steel.

After heating to 600°C there was a wide variation in the measured desorption coefficients from metal to metal. For Inconel 600 already at 500°C, the maximum temperature at which this sample was heated, all four desorption coefficients were in the $10^{-4}$ mol. electron$^{-1}$ range or below while for OFHC copper only $\eta_{\text{CH}_4}$ was in the $10^{-4}$ mol. electron$^{-1}$ range, the others being in the high $10^{-3}$ or low $10^{-2}$ mol. electron$^{-1}$ range. The values for the other metals lay between these two extremes.

4.1 SURFACE COMPOSITION

Complementary to a measurement of what is desorbed from a surface by electron and ion bombardment is a knowledge of the composition of the surface. This is conveniently obtained by Auger electron spectroscopy which provides quantitative identification of the elements present in the first two or three monolayers of the surface. Auger spectra from the six materials studied here were taken at
room temperature (25°C) and after heating at 100°C steps for one hour from 100°C
up to 900°C for the 316 L + N stainless steel, the Inconel 600, the titanium alloy
and the OFHC copper, but up to 1000°C for the Inconel 718 and only up to 500°C for
the aluminium alloy. A separate experiment on identically prepared samples
established that after this first hour the spectra showed little further change even
when heating for 24 hours. The temperature dependence of the surface composition
of 316 L + N stainless steel, Inconel 600 and Inconel 718 has already been pub-
lished by the authors 10), but for completeness the results are included in this
report along with the Auger spectra for the titanium alloy, the OFHC copper and
the aluminium alloy. These series of Auger spectra are shown in Figures 7, 8, 9,
10, 11 and 12. On all six metals a major contaminant observed was C whose Auger
line shape indicated that it was in the form of graphite 11). Traces of S, Cl and
Ca were also observed on some metals. The O is not considered to be a true
contaminant but is a normal component of the metal surface which is, of course,
unavoidably oxidised. Initially the underlying metals such as Ni, Fe, Ti, Cr and Al
were partly or wholly obscured since the surface layer of C and O prevented the
escape of their Auger electrons.

4.2 316 L + N STAINLESS STEEL

After the solvent cleaning the major contaminant on the stainless steel
surface was C (≈ 61 at.% as shown by the top spectrum of Fig. 7. From the
shape of the C peak it appears to be graphite. There was also ≈ 19 at.% O on the
surface and traces of S and Cl. Heating the sample to 300°C produced almost
no change in the surface composition except that chromium was more in evidence.
After heating to 400°C and 500°C a decrease in both the O and Fe content
of the surface and an increase in the chromium concentration was observed. The
C concentration remained relatively static. From 600°C up to 900°C the C and O
peaks decreased becoming undetectable at 900°C. However, at 600°C, P and S
appeared on the surface having diffused from the interior. At 900°C a C and O
free surface is obtained but with bulk S segregated at the surface. The S peak
height after heating to 900°C corresponds to about 11 at.% At 800°C and 900°C
the constituents of the stainless steel i.e. Ni, Fe and Cr are clearly seen.

4.3 TITANIUM ALLOY (Ti 6 Al 4 V)

Before heating and after cleaning the main surface contaminant was once
more C in the form of graphite (≈ 49 at.%) as shown in Fig. 8. The O surface
concentration was ≈ 19.7 at.% and there were also traces of Ca (1.65 at.%) and
Si (3.15 at.%). Heating to 300°C produced little change in the surface composition
except that the C concentration decreased slightly (≈ 40 at.%). After heating
to 400°C the O surface concentration decreased sharply to ≈ 5 at.% and the C
peak changed its shape to that of carbide. In addition, S started to diffuse from the bulk and appear on the surface. Heating to 500°C, 600°C, 700°C and 800°C further reduces the C and O peaks but results in an increase in the S surface concentration to about 24 at.% at 800°C. From 500°C the Ti and V peaks are evident and the low energy Ti peak at 27 eV, whose presence indicates that the Ti is near the surface, is also observed.

4.4 **INCONEL 600**

On the Inconel 600 surface (Fig. 9) the major contaminant was again C (= 18 at.%) in the form of graphite. Ca (= 16 at.%) was also present, there was 33.5 at.% O and traces of Cl (= 2 at.%).

Heating from 25°C to about 600°C produced relatively little change in the surface composition of the alloy. There was a gradual decrease in the O peak height and an increase in the C peak height to between 40 and 60 at.%. From 300°C the Cr peak became evident.

Heating to 700°C, 800°C and 900°C produced the most dramatic change in the Auger spectra. The O surface concentration dropped sharply from 700°C eventually being undetectable at 900°C. The C peak was just visible at 900°C.

From 600°C and upwards the S surface concentration increased rapidly having diffused from the interior and segregated at the surface. After heating to 900°C for 1 hour there was = 13 at.% S on the Inconel 600 surface. Also at 800°C and 900°C traces of P (= 2 at.%) were observed.

4.5 **INCONEL 718**

On Inconel 718 (Fig. 10) after the chemical solvent cleaning, C in the form of graphite (= 26 at.%) was the main impurity. There was = 39 at.% O on the surface and traces of Ca (= 1.5 at.%).

Heating to 800°C produced relatively little change in the surface composition. C was still present and, if anything, had increased slightly (= 35 at.% and the O had decreased (= 29 at.%). Heating to 900°C and 1000°C produced a dramatic change. The O and C peaks had virtually disappeared revealing the underlying Ti, Cr, Fe and Ni. However, as in the stainless steel, P and S had diffused from the bulk and segregated at the surface. After heating to 1000°C there was = 13 at.% P and = 4 at.% S on the surface.
4.6 COPPER OFHC

The top spectrum of Fig. 11 shows the composition of the OFHC copper surface after chemical solvent cleaning. The high and low energy Cu peaks were very evident and the main contaminant was once more C in the form of graphite (≈ 43.7 at.%) with traces of Cl (≈ 3.6 at.%), N (≈ 0.85 at.%) and S (≈ 0.38 at.%). After cleaning the O surface concentration was ≈ 8 at.%.

Heating to 100°C, 200°C and 300°C caused at first an increase in the Cl peak followed by a reduction at 300°C. The S concentration gradually increased to ≈ 2.2 at.% at 300°C and the C concentration also increased to ≈ 48.7 at.%.

At 400°C the O concentration started to decrease (≈ 4.6 at.%), the C had decreased (≈ 2.9 at.%), the Cl had disappeared but the S had increased to 10.3 at.%.

Heating to 500°C, 600°C, 700°C and 800°C produced further decreases in the O and C concentrations until at 800°C they were undetectable, but at 800°C there was ≈ 10.8 at.% S on the surface.

4.7 ALUMINIUM ALLOY (5086)

On the aluminium alloy surface after cleaning the main impurity was Si (≈ 25.1 at.%) followed by C (≈ 20.3 at.%) in the graphite form (Fig. 12). There was ≈ 54.6 at.% O present.

Heating to 400°C caused the Si concentration to decrease (≈ 1 at.%) but the C concentration increased to about 66%. The O concentration also decreased from its initial value of 54.6 at.% to 35% at 400°C.

After heating to 500°C the C concentration decreased somewhat to ≈ 58.5 at.% and the O increased to 41.4 at.%. Due to this overlying C and O the Al peak at 68 eV was not evident.
5. DISCUSSION AND CONCLUSION

There appears to be no obvious correlation between the surface composition
as determined via Auger electron spectroscopy and the number of molecules desorbed
per incident electron or ion as a function of temperature. Between room
temperature and 500°C or 600°C for all the metals except OFHC copper, the surface
contaminant concentration, i.e. the C and O peak heights, barely changes but the
electron and ion induced desorption coefficients for the C and O based molecules
change by between one and three orders of magnitude. In OFHC copper the C and
O peaks diminish from 400°C but between 25°C and 400°C the electron and ion
induced desorption coefficients decrease by factors of 50 and 4 respectively.

If one assumes that the desorption coefficients are proportional to the
surface coverage of the desorbed species, then changes of orders of magnitude
should be noticeable in the Auger peak heights for coverages up to one monolayer.
But, the escape depth of the Auger electrons is only of the order of 10 to 15 Å
or two to three monolayers, hence the Auger system only "sees" the top two or three
monolayers. This points to a possible explanation for the difference between the
Auger measurements and the desorption results. On the surface of our metals the
contamination layer is thick, i.e. in excess of three monolayers and the desorption coef-
ficients, but not the Auger signal, may depend strongly on the thickness of this layer.
This dependence on thickness is also observed for layers of condensed gas
(< 3 monolayers) on cold substrates 12). Moreover, the measurements of Calder
et al. 13) have shown that the equivalent of 70 monolayers of contamination,
mainly in the form of CO, may be desorbed by ion bombardment from a 316 L + N
stainless steel surface. But, obviously a layer of CO as thick as that cannot exist
on our surface at room temperature.

But, with a little modification our explanation may be valid if we consider
that the real surface, unavoidably oxidized, is not smooth but contains many micron
sized cracks and crevices 7,14) and if, in addition, the surface is porous with
holes whose dimensions are in the tens of Å range. The 70 equivalent monolayers
then be accommodated in such a structure. With increasing temperature this might
sponge-like surface could gradually deplete by diffusion to the surface or to
the interior and although the desorption coefficients decrease due to the
depletion of the sponge-like layer, it is not until the last two or three
monolayers begin to disappear from the surface that the Auger spectra start
to change.
The similarity in magnitude of both the electron and ion induced desorption coefficients and their temperature dependence for the different materials may also be explained in terms of the structure of this surface oxide layer. The surface (oxide) layers of the different metals may have a similar porous structure providing a reservoir in which the $H_2$, $CH_4$, CO and CO$_2$ are trapped, this trapping being of a physical nature and somewhat independent of the base material.

An alternative explanation may be that most of the C seen by the Auger spectrometer really is in the form of graphite and only a very small contribution to this peak comes from the CH$_4$, CO and CO$_2$. In this case changes in the coverage of these species would be difficult to detect against the large background signal from graphite.

Of course, the state of these desorbable gases on the surface is unknown. Do they exist in the molecular form or as dissociated molecules? Surface analysis via ESCA or electron energy loss spectroscopy could provide information on this question.

Apart from Al, which was only heated to 300°C, the other metals were, even after heating to 600°C for 24 hours in vacuo, still not clean; i.e. under electron and ion bombardment $H_2$, $CH_4$, CO and CO$_2$ were still desorbed. The Auger spectra showed that the metals would have to be heated to still higher temperatures of $\approx$ 900°C or 1000°C before a relatively C-free and presumably a surface free of CH$_4$, CO and CO$_2$ would be obtained.

It should not be overlooked that a surface which appears to be relatively clean under electron bombardment, (i.e. low electron desorption rates) can have desorption coefficients $\approx 10^2$ times higher for K$^+$ ions of the same energy - an observation which once again emphasises the arbitrary nature of 'cleanliness' which must be defined using the appropriate measuring method.
REFERENCES


8. Marie-Hélène Achard, CERN-ISR-VA/76-34.


FIGURE 1
Figure 4
FIGURE 5
Figure 6

Aluminium alloy

e^+ 600 eV

H₂, CO₂, CO, CH₄

Temperature (°C)

Molecules/ion (µ)

Aluminium alloy

K' 1400 eV

H₂, CO, CO₂, CH₄

Temperature (°C)

Molecules/ion (µ)
FIGURE 8