16th IUVSTA Workshop

Outgassing properties of materials:

The kinetics and thermodynamics of adsorption, desorption and passivation

April 6-10 1997

Scope:

To obtain a coherent picture of outgassing properties of materials in vacuum, by bringing together scientists interested in vacuum, surface and bulk material properties.

Topics:

- Summary of outgassing measurements.
- Exotic materials in UHV and XHV.
  - -- Polymers, ceramics...
  - -- What is the practical limit for sustainable vacuum (UHV-XHV)?
- Grain boundary diffusion.
  - -- Morphology-related topics.
- Defects.
  - -- The influence of defects on outgassing properties.
- Diffusion barriers.
  - -- Creation, removal and the influence of diffusion barriers.
- The inverse problem; gas purification.
  - -- Selective absorption, surface activation.
  - -- Combination of surface and bulk properties of different materials.
- Adsorption-desorption, detailed balance (including photo-assisted processes).
- Outgassing simulation and experiments in outer space.
  - -- Common problems, or reversed problems?
- Pressure and composition determination of residual gases.

Panel discussions on all topics.

Organizers:

B. Hjörvarsson and L. Westerberg

Scientific committee:

J. Greene, B. Hjörvarsson, B. Kasemo, A. Kleyn, and L. Westerberg.

Final Report on the 16th IUVSTA workshop Outgassing properties of materials: The kinetics and thermodynamics of adsorption, desorption and passivation

Gräftåvallen, near Östersund, Sweden 6-10 April 1997

Fred Dylla[1], Björgvin Hjörvarsson[2], Aart W. Kleyn[3] and Lars Westerberg[4]

[1]Jefferson Lab, 12000 Jefferson Avenue, Newport News, VA 23606, USA
[2]Department of Physics, Box 530, S-751 21 Uppsala, Sweden
[3]FOM-Instituut voor Atoom- en Molecuulfysica, Kruislaan 407, 1098 SJ AMSTERDAM, NL
[4]The Svedberg Laboratory, Box 533, S-751 21 Uppsala, Sweden

This workshop was the 16th in series sponsored by various Divisions of the International Union of Vacuum Science, techniques and Applications (IUVSTA). It was initiated by the Vacuum Science Division and co-sponsored by the Surface Science Division of IUVSTA in order to strengthen the connection between researchers working on applied problems and those studying the corresponding phenomena at a basic level. The scope of this meeting was to obtain a coherent picture of outgassing properties of materials in vacuum by bringing together scientists interested in vacuum, surface and bulk material properties. The workshop was sponsored and hosted by the Swedish Vacuum Society. Financial support from IUVSTA, The Royal Swedish Academy of Sciences through its Nobel Committees for Chemistry and Physics, Swedish Natural Research Foundation and Swedish Research Council for Technical Sciences is greatfully acknowledged. Thanks to this support, full financing was obtained for the invited speakers and supports could be given to 4 participants from Eastern Europe.

The meeting was held at Gräftåvallen, near Östersund, Sweden, in a remote mountain location. In addition to the scientific programme held in the mornings, late afternoons and evenings, time was available for various outdoors activities, often related to snow, and a concert. The local organisers were Lars Westerberg, Hjörgvin Hjörvarsson with the help of conference secretary Inger Ericson (all at Uppsala University). The other members of the organising committee were Bengt Kasemo (Chalmers university of Technology, Sweden), Joe Greene (University of Illinois at Urbana, USA) and Aart Kleyn. There were 42 participants from 14 countries, with appreciable participation from Germany, Italy, Japan, the Netherlands, Russia, Sweden, and the USA.

Fifteen invited talks were presented at the meeting. F Dylla, A Kleyn and U Gelius were invited to be responsible for the summary session. In addition to this, 14 contributed talks were presented at the workshop that added supporting material to the invited talks. E. Karlsson (Uppsala, Sweden) gave a late evening talk on Classical and Quantum Transports in Solids. Here follows a list of the invited speakers and their titles:

- **F. Dylla (Thomas Jefferson National Accelerator Facility, Newport News, USA): Summary of outgassing measurements.**
- **R. P. Redhead (NRC Canada): Modelling of Outgassing andthe Limits of Sustainable Vacuum (XHV-UHV).**
- **A Wildes (Australia, pres. at IFM Linköping, Sweden): Passivation of Y!**
- **D. Manos (Williamsburg, VA, USA): Outgassing from Polymers.**
- **E. Murad (Philips Labs, MA, USA): Adsorption, Desorption and Outgassing on Spacecraft.**
- **I. Zoric (Chalmers, Sweden): Dynamics of Adsorption and Collision Induced Molecular Processes on Surfaces.**
- **W. Lanford (SUNY Albany, USA): Hydrogen and the Weldingof High Strength Steel.**
- **R. E. Pedder (ABB Extrel, Pittsburgh PA, USA): State of the art Residual Gas Analysis.**
- **T. Dickinson (Washington State University, Pullman, USA): Desorption and Photo-Desorption from ionic surfaces, Role of defects.**
- **R. Kirchheim (Univ. Göttingen, Germany): Interstitial Diffusivity in Defected and Amorphous Materials; Hydrogen Diffusion along Grain Boundaries.**
- **M. Sancrotti (Lab. Nationale TASC-INFM, Trieste, Italy): Gettering Materials Investigated by Means of Surface Sensitive Techniques.**
- **Y. Ishikawa (Hitachi, Ibaraki, Japan): Outgassing, Hydrogen Diffusion Behaviour and Surface Characterization of Stainless Steel.**
- **F. Dylla for R. Weiss (MIT, MA, USA): Outgassing treatments andanalysis for the Laser Interferometer Gravity Observatory (LIGO).**
- **N. Hilleret (CERN, Geneva, CH) Outgassing in large accelerators: An operationnal experience. IUVSTA Workshop Summary**

From the lively discussions at the workshop and these summaries one can definitely conclude that the topic of outgassing from materials is far from beeing sufficiently understood and relevant experimental data are available to vacuum users. It has already been discussed in the IUVSTA divisions to arrange another meeting in this field in about three years time. After this follows some detailed comments by Kleyn, Dylla and Hjörvarsson:

Comments by Aart Kleyn:

Recurrent topics seen at the workshop were:

- **the nature of the surface including questions as how many atomic layer before vacuum are relevant to the outgassing process; what is the nature of capping oxide of a degassing material.**
- **Sticking probabilities with questions such as why do first principles calculations not reproduce experimentally observed activation barriers for O2/Al(111) and O2/Ag(111), and why are sticking probabilities found in applied work lower than anticipated from surface science work.**
- **Adsorption isotherms, such as Henri's law, BET, Freundlich, DRK, Temkin appeared to have very limited value even though in some cases using the Clausius-Clapeyron equation 'surface science' adsorption energies could be recovered.**
- **Desorption mechanisms: thermal desorption is most relevant in most practical cases. A very important question here is what are active sites for recombinative desorption, and how can they be passivated. In the accelerator community photon stimulated desorption (synchrotrons!), electron or ion induced desorption were very relevant. In case of spacecraft orbiting in high vacuum reactive desorption, possibly caused by direct, Elea Rideal reactions and leading to 'shuttle glow' is very relevant.**
- **Diffusion: this determines outgassing from the bulk of materials. It is most relevant for hydrogen. This brought in some solid state physics into the meeting. Important issues are diffusion barriers, mobile and immobile hydrogen and crack diffusion.**
- **Residual Gas Analysis: in general good measurements can be carried out with the possible exception of measurements on spacecraft yielding atmospheric composition data, due to surface reactions in the ioniser.**
- **Engineering design could be formulated, especially for the design for small systems. For large vacuum systems dedicated research seems necessary. Especially in case the size and the handling of the system makes bake-outs unpractical. Lots of empirical data is compiled in 'phone books'.**
- **Particle of the meeting was without any doubt hydrogen. This atom is hardest to remove in vacuum systems because it is very mobile and can be dissolved in bulk materials. It strongly influences materials properties. There were common detection problems: in welding studies hydrogen bubbles with the sample under oil were used for detection. Nuclear reaction analysis works very well and provides depth resolution, but is not easily accessible. Thermal desorption spectroscopy in vacuum is presumably the best practical method to detect hydrogen in the near surface region.**

Comments by Fred Dylla:

To summarize the technical program of the workshop, comments are given below on the topics of (1) outgassing measurements; (2) the relationship between surface conditions and outgassing; (3) the status of modelling of outgassing phenomena; and (4) suggestions for future work to simulate progress in this field.

Outgassing Measurements.

There are two methods which have been used to measure outgassing rates: (1) the throughput method and (2) the rate-of-rise method. The throughput method relies on sampling the outgassing from a well defined area and volume of sample through a well defined pumping aperture. The rate-of-rise method relies on isolation of the test volume from all pumps followed by measurement of the pressure rise per unit time under zero pumping speed conditions. Both methods have their limitations which became topics of considerable discussion at the workshop. Recent theoretical analysis by Redhead and measurements by Akaishi and Edleman have reemphasized earlier work in the literature (which is often overlooked) that enumerates under what conditions the throughput method can lead to outgassing rates that are dependent on the pumping speed and a sizable underestimate of the true outgassing rate of the material under question. The relevant system parameter is the area ratio divided by the low coverage sticking coefficient. For the system of most practical interest : water outgassing from technical surfaces (stainless steel and aluminum), many of the literature measurements may fall into this regime making a comparison of literature values more difficult. Key questions that developed from this discussion were the value of the sticking coefficient of water on stainless steel, and the nature of the adsorption sites and kinetics (i.e., appropriate isotherm) for this important system.

The rate of rise method avoids the above difficulty at first glance; however if the method is pursued over many orders of magnitude in pressure rise than the adsorption/desorption characteristics of the outgassing molecule may change with pressure. The desorption of hydrogen from stainless steel should be a relatively simple system to measure, analyze and understand. The diffusion coefficient of hydrogen is large in steels and a large data base is evident in the literature. Measurements of outgassing of hydrogen from stainless steel given by Jousten at the workshop show a linear slope for 6 orders of magnitude in pressure. Hydrogen is thus acting as a non-adsorbable gas in this circumstance with a vanishingly small sticking coefficient.

Relationship between surface conditions and outgassing

A significant topic of discussion at the workshop was the relationship between the surface structure and chemistry of a material and the observed outgassing rate. Very little data have been gathered on this topic for practical materials, although there is a rich database on well characterized model systems (often single crystal) in the surface science literature. For the case of stainless steel, the composition of this oxide has been characterized in several studies by conventional sputter profile techniques. Correlation of these data with subsequent outgassing behavior has not proven useful. For example, a large selection of recent data on stainless steel outgassing was shown by Ishikawa that included a variations in the oxide layer thickness and chromium content as the bakeout temperature was changed from 100oC to 450oC. When the data is displayed from a large set of measurements, no trend is evident. However, when one data set is selected which is constrained to variation of only one parameter on one sample type (i.e., systematically growing the oxide layer thickness or enriching the near surface chromium content, then a more systematic trend is observed. A related topic from this discussion is the choice of bakeout temperature to minimize the outgassing from stainless steel. There is at present no clear answer to this question. In fact, the present situation may be even more confused by recent data presented at the workshop. For a variety of treatments described by Ishikawa, all resulted in very low outgassing rates (<<10-11 Pa.m2/s), and there was no clear advantage to the higher temperature bakeouts. Jousten also showed a study that indicated somewhat lower outgassing rates with lower temperature (100-200oC) treatments. Questions were raised concerning more detailed characterization of the passivation oxide layer. Ishikawa presented a beautiful

series of micrographs and depth profiles of stainless steel taken with a field ionization atom probe. The micrographs allowed full 3D elemental analysis with atomic resolution. One example showed the changes in the oxide layer as a steel sample was heated and oxidized in pure oxygen.

Modelling of Outgassing

Traditionally, modelling of outgassing phenomena has involved two types of models where either diffusion of the outgassed species (or a precursor) or desorption of the outgassed species was considered as the rate-limited step. Redhead presented his recent analysis of the outgassed of water from stainless steel as being desorption limited and described with a modified Tempkin isotherm. The model fits well with the data of Li and Dylla, who used a diffusion limted model to describe the data. Hence, another of the thought provoking questions posed at the workshop was: what is the rate limiting process for the adsorption/desorption of water on steel surfaces? An understanding of this simple question has significant practical significance considering the number of vacuum systems in use for scientific and industrial applications that are exposed to ambient conditions and not baked. For this case, it is likely the kinetics involves an interlinkage of several processes: diffusion of water or water precursors (H, OH) through the oxide layer to the surface (perhaps through pores or grain boundaries connected to the surface); recombination on the surface; and finally, desorption from the adsorption or recombination site to the gas phase.

The case of hydrogen diffusion may be more simple to understand and model. Redhead presented a model that has hydrogen diffusing from the bulk steel, recombining on the surface at a site that is not accessible to surface adsorption of hydrogen. These later sites need a surface density less than 1011 cm2 to account for the low sticking coefficients that the rate-of rise outgassing measurements (noted above) imply.

Suggestions for Future Work

- **The above discussions on the state-of-the-art of the measurements and theoretical understanding of outgassing phenomena generated a number of interesting suggestions for future work to stimulate progress in the field:**
- **Better correlation between outgassing measurements and the morphology and chemical structure of the surface and near surface layers.**
- **Identification of the chemical state of H2O on or near the surface.**
- **Measurement of the sticking coefficient of H2O on practical surfaces (steel and aluminum) as a function of surface conditions.**
- **Influence of deposited passivation layers (such as TiN, diamond-like carbon, etc.) on outgassing.**
- **Measurements and corresponding modelling of outgassing from model systems (simple metals, oxides, and polymers) that may contribute to the understanding of outgassing behavior observed with practical materials used in vacuum systems.**
- **Experiments that could identify and quantify the role of diffusion in the near-surface region of vacuum materials (what is the diffusant - H, CH, OH - and what are appropriate values for the defusion constant?)**

Thermal desorption spectroscopy measurements of H2 and H2O from model systems.

Clearly, more than enough work was identified by the workshop participants to keep research in this field quite active. The talks presented on large scale applications of vacuum in both basic science and industry provided significant impetus for advancing the state of our understanding of outgassing phenomena from a variety of practical materials.

Workshop participants are indebted to the members of the Swedish Vacuum Society who planned and hosted the workshop. In addition to the experience in the workshop conference room, our hosts at the Gräftåvallen Conference Center gave us the opportunity to participate in a number of unique experiments on stick-and-slip friction on frozen water surfaces in the slightly rarefied but most beautiful atmosphere of Gräftåvallen.

Additional comments by Björgvin Hjörvarsson:

The influence of the overlayer (metal-oxide) on the hydrogen uptake and release is nontrivial. The presence of an oxide layer can hinder the uptake as well as the release of hydrogen, which was illustrated by the deterioration of single crystal Yttrium films. By covering the surface by Gold, the catalytic splitting of water was enhanced and the Yttrium films demolished rapidly. Without any Au capping, this effect was negligible. These results have implications on the role of Cr-oxides on the surface of stainless steel, as the Cr oxides are catalytically inactive. The recombination and the dissociation of molecules is restricted to areas where the metal is exposed to the ambient. This has implications on the sticking coefficient, the dissociation as well as the recombination rate of hydrogen on water.