

Thursday Afternoon, October 18, 2007

Vacuum Technology

Room: 618 - Session VT1-ThA

Adsorption/Desorption Phenomena on Vacuum Materials

Moderator: N. Peacock, MKS Instruments, Inc.

2:00pm **VT1-ThA1 Surface Morphology and Surface Composition of Vacuum Fired Stainless Steel***, *M. Leisch*, Graz University of Technology, Austria **INVITED**

Stainless steel is one of the most used construction materials in vacuum technology. Especially in XHV applications a high temperature treatment (vacuum firing) is commonly used to reduce outgassing of this material. There is a considerable body of work on outgassing of hydrogen from stainless steel. The results are basically described by two models: the diffusion limited model and the recombination limited model. Since recombination is strongly related to surface morphology and composition, surface characterization has been performed by atomic force microscopy (AFM) and scanning tunneling microscopy (STM). The surface near composition has been measured by atom probe depth profiling analysis. After vacuum firing a significant change in surface morphology can be observed in AFM and STM. The high temperature treatment leads to a complete reconstruction of the surface. The recrystallization process leads to an increase of the overall surface roughness with deep grooves up to 1000 nm in depth at the grain boundaries. On top of the crystallites wide flat terraces over 100 nm in width bounded by bunched atomic steps and facets can be observed. The high resolution STM micrographs additionally show stacking faults and local defects on these terraces assigned to (111) planes. The atom probe depth profiling analysis on vacuum fired samples results in a noticeable surface enrichment of nickel and certain depletion of chromium in the first atomic layer. In the second atomic layer chromium enrichment was measured. From the knowledge of surface structure and surface composition a recombination limited outgassing is very unlikely. Comparison with experimental studies on hydrogen desorption by thermal desorption spectroscopy strongly support the explanation by the diffusion limited model. It can be assumed that subsurface defects form traps with different energetic levels. The increase in diffusion energy after emptying the higher subsurface levels may also explain the observed outgassing behaviour of stainless steel.

*Work supported by province of Styria, Austria Zukunftsfonds project P119.

2:40pm **VT1-ThA3 Monte Carlo Simulation of Temperature Programmed Desorption Including Binding Energies and Frequency Factors Derived by DFT Calculations**, *P. Thissen, O. Ozcan*, Max-Planck Institut for Iron Research, Germany, *D. Diesing*, Institut of Physical Chemistry Essen, Germany, *G. Grundmeier*, Institut of Macromoleculare Chemistry Paderborn, Germany

Temperature-programmed desorption (TPD) techniques are important methods for the determination of kinetic and thermodynamic parameters of desorption processes or decomposition reactions. A sample is heated with a temperature program $\beta(t) = dT/dt$ (with the temperature T usually being a linear function of the time t) and the partial pressures of atoms and molecules evolving from the sample are measured, e.g. by mass spectrometry. When experiments are performed using well-defined surfaces of single-crystalline samples in a continuously pumped ultra-high vacuum (UHV) chamber then this experimental technique is often also referred to as thermal desorption spectroscopy (TDS). A Monte Carlo model has been developed for describing the temperature-programmed desorption of adsorbates from single crystal surfaces. The developed Monte Carlo Program requires the input of frequency factors and unity bond order binding energies BE (for the top position) for every bond under examination. For the first time the required values are now calculated using a DFT code. The virtue of both methods (Monte Carlo and DFT) is combined in the present work. Our new model takes into account the effects of surface diffusion, the influence of surface-adsorbate (S-A) and adsorbate-adsorbate (A-A) interactions and the coverage dependence of the activation energy for desorption derived by precise calculations on an atomically defined level. The inclusion of localized (S-A) and (A-A) interactions has a pronounced effect on the shape of the predicted TPD spectrum. Only a single peak is observed in the absence of (S-A) and (A-A) interactions, whereas multiple peaks are found when these interactions are included. The inclusion of (S-A) and (A-A) interactions is also shown to produce a

nonlinear decline in the activation energy for desorption as a function of increasing adsorbate coverage.

3:00pm **VT1-ThA4 Temperature Programmed Desorption Measurements of the Binding Energy of Water to Stainless Steel Surfaces**, *J.H. Hendricks, P.J. Abbott*, National Institute of Standards and Technology, *P. Mohan*, NPL India, *J.P. Looney*, Brookhaven National Laboratory

The presence of water vapor is the limiting factor in achieving ultra-high vacuum (UHV) in an unbaked stainless steel system. While the "water problem" has been of scientific and technical interest for many decades, fundamental measurements of water interactions with stainless steel systems are not well characterized, including the binding energy and sticking coefficient of water on stainless steel. In addition, outgassing rate measurements of water from stainless steel surfaces are typically hampered by the problem of re-adsorption, leading to inaccurate measurement results. The NIST Pressure and Vacuum group has undertaken a study of the binding energy of water to stainless steel surfaces. A temperature programmed thermal desorption apparatus was constructed for this purpose and will be described in detail. The apparatus uses computer control to linearly heat a stainless steel filament at a rate of 3 °C/s while a quadrupole mass spectrometer detects the thermally desorbed species. The system is designed with a high pumping speed to minimize the problem of re-adsorption/desorption, and has reproducibly shown a water thermal desorption peak at 139 °C. A model for thermal desorption, first employed by Redhead in 1962¹ was used to determine the activation energy, or binding energy of water to stainless steel. This technique has reproducibly yielded a water binding energy between 25.6 and 26.0 kcal/mole. These results may justify lower baking temperatures than are traditionally used for achieving UHV. Future work will focus on the apparent interplay of water desorption and hydrogen desorption observed during UHV system bake-outs.

¹ Redhead, P.A., Vacuum, 12, 203 (1962).

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