A commercial gas analyzer adapted for thermal desorption studies

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ABSTRACT. A system for thermal desorption studies can be implemented very straightforwardly from a commercial instrument designed for gas analyses. The commercial instrument incorporates a quadrupole mass spectrometer and the vacuum station to operate the spectrometer. The instrument is modified with a stainless steel six-way cross device which accommodates a sample manipulator, a leak valve and an Ar sputtering gun. The sample foil is resistively heated with very linear rates using a custom made power supply. Descriptions of the custom made sample manipulator and power supply are given. Results of hydrogen and carbon monoxide desorption from palladium foil are discussed.

RESUMEN. Un sistema para estudios de desorción termal puede ser implementado muy fácilmente a partir de un instrumento comercial diseñado para análisis de gases. El instrumento comercial consiste en un espectrómetro de masas, tipo cuadrupolar, y su sistema de vacío donde se opera el espectrómetro. El instrumento se modificó con una cruz de seis vías, de acero inoxidable, donde se pueden acomodar un manipulador de muestras, una llave de dosificación de gases y un cañón de argón para limpieza de la muestra. Esta última, en forma de lámina delgada, puede ser calentada por medio de una corriente eléctrica, en forma muy lineal, proveniente de una fuente fabricada en el laboratorio. Se dan en este trabajo la descripción del diseño del manipulador de muestras y de la fuente de poder. Se dan y se discuten también los resultados obtenidos de desorción de monóxido de carbono e hidrógeno de paladio.

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1. INTRODUCTION

Thermal desorption is a useful technique to characterize adsorption states of molecules on solid surfaces. This technique has undergone several stages since its earliest creation, using metallic filaments, glass chambers and pressure gauges for gas detection. This technique was first described by Apker [1] in 1948 and many studies were successfully completed by Ehrlich [2]. A very good review about the application of this technique to solve many problems in basic science was written by David King [3].

At present, this technique is normally performed in stainless steel vacuum chambers which incorporate expensive surface analysis tools (see, for example, Ref. [4]). There is

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no commercial system that can be obtained off-the-shelf to carry out thermal desorption experiments. Companies which specialize in the surface analysis market do not offer the option of an integrated system for thermal desorption studies ready to be used. Consequently, only the researchers with experience in this technique are able to build a new system when the need arises again. The purpose of this paper is to make aware researchers with no experience in thermal desorption, but interested in implementing the technique in their laboratories, that a system can be assemble with off-the-shelf components, little frustration and a modest budget.

Recent advances in electronics, vacuum pumps designs and computers make it possible to build a rather inexpensive system for thermal desorption studies. These studies are useful in other areas beside studies of gas desorption from well characterized single crystals. There is a need for gas evolution systems in areas of solid state physics such as high temperature superconductivity [5] and electronic quantum effects studies of nanostructures [6], among others. A system like the one described in this paper may fill the instrumentation gap between expensive ultra-high vacuum [4] and very limited small systems like the one described in Ref. [5]. The main limitation of many designs used for gas evolution systems, is that the mass spectrometer is located down-stream and the gas is sampled through a valve for analysis. A designs like that creates a diffusion limitation at the sampling valve and the true kinetics of the phenomenon studied can not be obtained with the mass spectrometer.

2. DESCRIPTION OF APPARATUS

A. Vacuum system

The system was built starting from a modified AMETEK (Thermox Instruments Division, Pittsburgh, Pennsylvania) instrument for gas analysis. This instruments consist of a vacuum system mounted on a mobile cart which incorporates a Dycor Quadrupole Gas Analyzer. This instrument is equipped with a Balzers 50 l/s Turbomolecular pump backed with a Leybold Trivac S/D 1,6 B mechanical pump.

The modification to the instrument was to include a 6-way cross with 2.75 in ConFlat flanges (MDC High Vacuum Components, California) on top of the Turbomolecular pump. The 6-way cross allows us to place a sample manipulator, an Ar ion sputtering gun, the quadrupole mass spectrometer, a Varian variable leak valve and a glass view port on the other available flanges. A schematic diagram of this arrangement is displayed in Fig. 1. The base pressure of the system after outgassing stayed in the middle 10^{-9} torr.

B. Sample manipulator and sample heating

A simple sample manipulator was also made with a modified 6-way cross obtained from MDC. Four ways of the cross were reduced in size (1.33 in conflat flanges) to accommodate feedthroughs for a thermocouple and for high current connections. Two 0.32 cm in diameter copper bars were mounted a rotary feedthrough (also obtained from MDC) using two pieces of alumina ceramics. These copper bars were connected to the high current

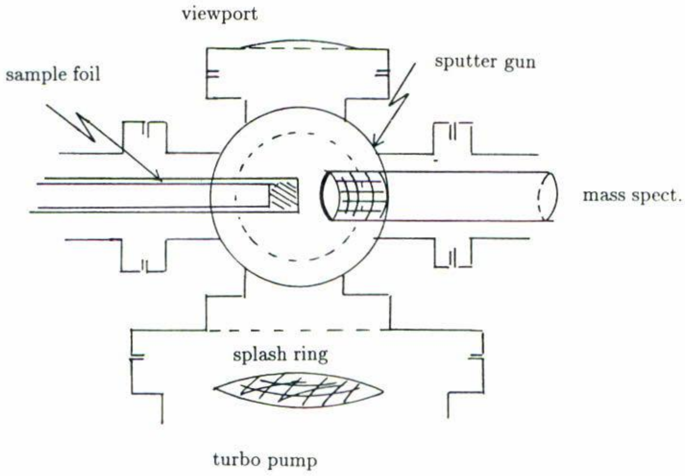

FIGURE 1. Schematic diagram of vacuum chamber consisting of a six way cross with 2.75 in conflat flanges. This diagram shows a cross section of the chamber with some details of the sample foil and spectrometer head.

copper feedthroughs using braided copper wires insulated with flexible ceramic sleeves. The sample in the form of 1×1 cm metal foil can be placed at the end of the copper bars using two pieces of 0.09 cm in diameter metal wires which are spot welded to the foil.

A thermocouple which allows to monitor the sample's temperature, can be made with 0.013 cm in diameter chromel-alumel wires which are connected to the thermocouple feedthroughs. The temperature measured with this thermocouple was compared with readings from an optical pyrometer in the range of 600–800 degrees Centigrade. The temperatures agreed well withing +2 degrees. This configuration for the manipulator allows the sample to be rotated in 360 degrees and consequently exposure of both sides to Ar ion sputtering is achieved. A diagram of the sample manipulator is displayed in Fig. 2.

The sample was resistively heated using a high-current ac power supply. This power supply was built using a controller/programmer, model 821 and an SCR assembly, model 831, both obtained from Eurotherm Corporation (Reston, Virginia). The output of the SCR assembly was delivered to a high current transformer (Reggio, Santiago, Chile) which converted the 220 V to a 5 V, high amperage pulse. The transformer is capable of delivering 100 A current. An electronic diagram for this power supply is shown in Fig. 3. This power supply was able to heat the sample, from room temperature to 1000 degree C, in a few minutes with very linear rates from 2.5 up to 20 degree/s. More details of the performance of this power supply can be found elsewhere [7].

Heating the sample with very linear rates is fundamental in these experiments for an easy analysis of the desorption curves. An example of temperature ramps obtained with the system using a heating rate of 5 and 10 degree C/s are displayed in Fig. 4a and 4b.

C. Thermal desorption analyses using the mass spectrometer

A Dycor M100M quadrupole mass spectrometer was used to monitor H_2 and CO desorbing from a piece of Pd foil. The control unit of the mass spectrometer was connected to

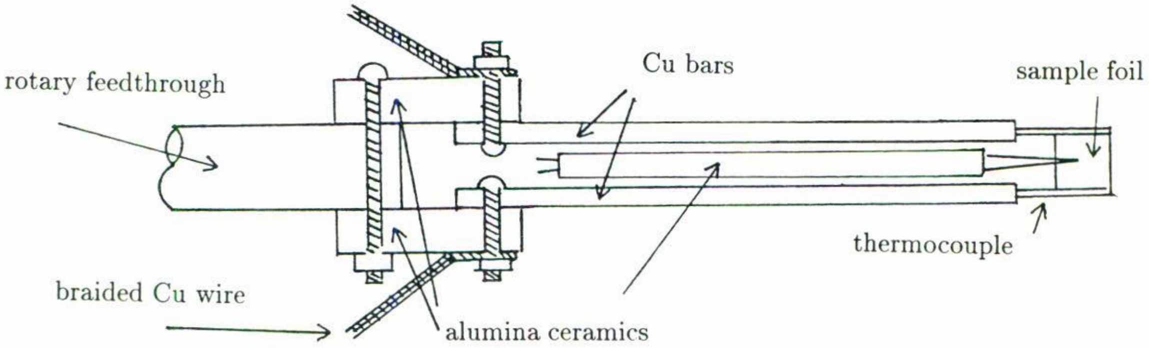

FIGURE 2. Schematic diagram of sample manipulator consisting of a modified 6-way cross and a rotary feedthrough. The feedthrough for thermocouple and current connections are mounted on 1.33 in conflat flanges. The ceramic insulators that connect the two copper bars with the rotary feedthrough are flat in shape. The ceramic used as insulation for the thermocouple wires is rounded and contains two separate holes for the wires.

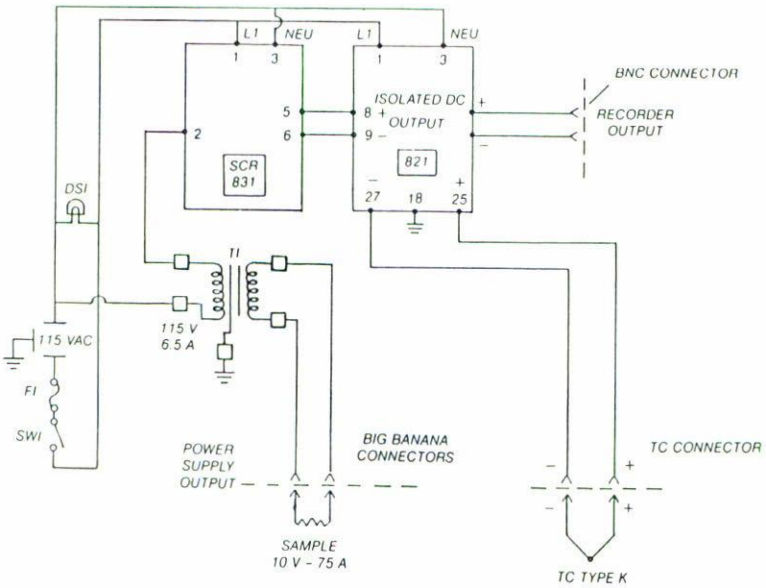

FIGURE 3. Schematic diagram of the power supply built to generate linear heating ramps.

a PC-AT 286 computer through an RS232 serial port. The desorption spectra can be obtained in a time display mode and stored in the memory of the control unit for later data download to the computer. Typically, four masses are monitored for 120 or 180 s, with a sampling rate of a point every 0.8 s. At the same time the temperature is registered using real time acquisition of LabTech Notebook (Laboratory Technologies Corporation, Wilmington, Massachusetts). This software coupled with 6B modules from Analog Devices (Norwood, Massachusetts), allows acquisition of voltage or current signals with variable sampling rates.

The data can be transferred for further analysis and plotting in the spreadsheet of

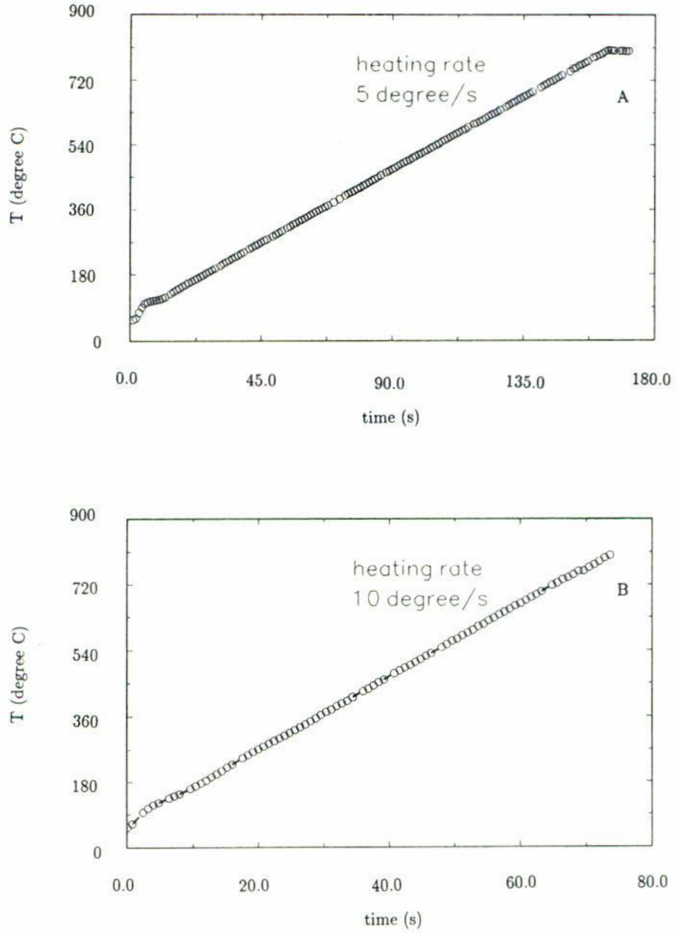

FIGURE 4. Plots of sample temperature as a function of time for a 1 × 1 cm thin Pd foil heated with a rate of: a) 5 degree C/s; and b) 10 degree C/s.

any program similar to Lotus 123 (Lotus Development Corporation, Cambridge, Massachusetts).

Typical spectra of CO and H_2 desorbing from a piece of 1×1 cm Pd foil, obtained with the system described in this paper, are displayed in Figs. 5a and 5b. The Pd sample was exposed to either 500 L of H_2 or CO exposure, before the TDS spectrum was obtained.

The CO TDS qualitatively agrees well with previous studies of CO desorption from Pd (100) using the same technique in a conventional ultra high vacuum system [8,9]. In that work, Ertl and coworkers show that a main CO peak appears around 200 degrees C (desorbing from Pd) while a smaller peak (due to CO adsorption from surface carbon) appears as a shoulder around 100 degrees C. The shape of the CO curve obtained in this work is exactly the same obtained by Ertl and coworkers from a Pd surface slightly contaminated with carbon. The H_2 signal is at least 5 times larger than the CO signal for the same exposure, since Pd absorbed H_2 in the bulk.

The interpretation of these results is given below. Hydrogen readily diffused in the palladium and desorbes as one broad peak at about 350 degrees C. The desorption traces

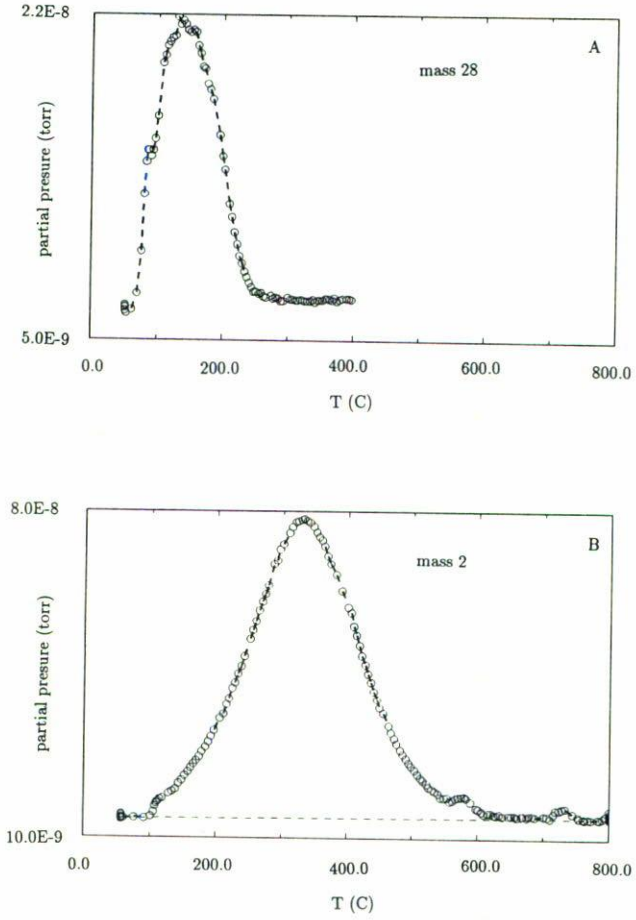

FIGURE 5. TDS spectra for: a) CO desorption from Pd foil after exposure to 500 L of CO and using a heating rate of 10 degree/s; and b) H_2 desorption after exposure to 500 L H_2 and using a heating rate of 5 degree/s.

can be fitted with near Gaussian curves and plots of the ln(rate) versus inverse absolute temperature are straight lines only if the desorption order $n = 1.25$. An activation energy of about 8.5 Kcal/mol is obtained for this subsurface absorption. Carbon monoxide is adsorbed, as two states, on the surface of the foil and complete coverage is quickly reached below 100 L. Analysis of these curves in order to obtain kinetic parameters is described in details elsewhere [10,11].

3. SUMMARY

A rather inexpensive apparatus with very good vacuum characteristics can be assembled with off-the-shelf components. Data acquisition is obtained with an inexpensive computer and available software. The system is flexible enough to allow further modifications to suit more specific needs. This system can be dedicated to thermal desorption studies on well characterized single crystals or polycrystalline foils or wires. The system can be used to study sublimation of thin films or any other phenomenon associated with gas release from solids, such as evolution of oxygen from high T_c superconductors. This system is ideally suited for research in places where resources are scarce (such as liquid nitrogen or cooling water), since the only utility needed to operate the instrument is electricity.

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