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TITLE

Development of a nondestructive testing method and facility for investigation of surface reactions appearing in damage, corrosion, adsorption and catalytic processes encountered in the heat transfer systems of nuclear power plants and the energy storage problems

FINAL REPORT FOR THE PERIOD

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YOUR REF.:

OUR REF: 263/1-1986.

Zagreb, 21 July 19 86

Final report on the
RESEARCH CONTRACT 3227

entitled:

"Development of a nondestructive testing method and facility for investigation of surface reactions appearing in damage, corrosion, adsorption and catalytic processes encountered in the heat transfer systems of nuclear power plants and the energy storage problems",

and carried out at the Institute of Physics of the University Zagreb, with Dr.B.Gumhalter as the Principal Investigator. This report covers the time period from the commencement of the Project (1 August 1982) to its end (31 July 1986).

1. Introduction

This research contract provided a partial sponsorship for the research programme of the Institute's Surface Science Group which intended to direct its experimental activities towards the investigation of the problems of initial steps of oxidation, oxide layer growth and corrosion of metals and alloys used for construction of the nuclear power plant secondary heat exchange systems.

To meet the requirements of this programme the group had to make plans for a reconstruction of vacuum facility available at that time at the Institute, together with various subsidiaries needed for this type of research. At the time of the application for the research contract the Institute had at its disposal a high vacuum equipment (Varian VT 108) with 2 sorption pumps., 140 l ion pump, titanium sublimation pump and pressure gauges.

2. Rebuilding of the old highvacuum equipment

The old vacuum apparatus was improved and rebuilt in order to enable the achievement of ultrahighvacuum conditions, a prerequisite for any surface physics experimental work. All-metal valves, metal gaskets, metal-ceramics sealed feed-throughs, CF-flanges, and clamps (home made or purchased) had been mounted to the apparatus. At the same time a suitable sample holder was constructed and used for first testing. At the later stage of the development of the apparatus, this sample holder was replaced by more appropriate one. The pumping system (ion pump + sorption pumps) was also replaced in the third year of the project. New equipment was added to the apparatus: quadrupole mass spectrometer (Vacuum Generators), ion gun (Varian), turbomolecular pump (Balzers), rotary drive (Vacuum Generators), diode probe unit (home made), quartz crystal microbalance (partially home mode), bake-out system (home made), several power supplies (home mode), TDS programator (home made), leak lines (Vacuum Generators), sample holders of various types (home made), and evaporation units (home made). All details are described in the corresponding Progress reports and ref.1.

3. Experimental methods

From the very beginning of the project we focused our programme on introducing three surface sensitive methods: a) Quartz-crystal microbalance (QCMB), b) diode method for measuring the work function changes of a metal surface in interaction with a particular gas, and c) thermal desorption spectroscopy (TDS). Here we are going to review briefly the technical development of these techniques in our laboratory.

a) Quartz-crystal microbalance:

QCMB is a technique suitable for measuring the kinetics of thin metal film deposition and gas adsorption. At the very beginning of the project the QCMB was mounted in the following way: the crystal itself was mounted on a copper block and isolated by the use of special sapphire spacers. Sapphire was used in order to improve heat exchange at very low temperatures. The copper block was mounted on linear motion drive (LMD) with the crystal face pointing toward the evaporation unit.

Temperature stabilization was established by a continuous flow of tap water through LMD feedthroughs. Temperature was measured with chromel-alumel thermocouple screwed to the copper block. The crystal was connected with Colpitt oscillator (produced and donated by Chalmers University, Götteborg). The frequency was measured with 7226EV/Kit 10MHz Universal Counter (Intersil). The first measurements of the deposition rate of nickel thin films showed the inability of the frequency counter to measure frequency shifts resulting from adsorption of a monolayer of oxygen. This problem was solved by the addition of an extremely stable 10MHz frequency generator (Rhode Schwarz) combined with a signal mixer and signal-difference divider.

A simple evaporation unit for this film deposition on QCM was produced in such a way that the simultaneous evaporation from two sources was possible.

b) Diode probe for the work function change measurements is based on the scheme given in a paper by Christmann et al.² The basic electronics, filament holder and filament power supply were produced by the Institute workshops. The measuring electronics worked in constant voltage regulated operation mode, typical values being $U_{fil} = 1-2V$, $I_{fil} = 0.7-1.A$, with diode current of $40 \mu A$. The stability of the probe was not good enough because of i) mutual interactions of all the electronic items involved in the measurements, and ii) filament instability when operating in the oxygen atmosphere. A great effort has been taken to prepare filaments which were both resistive to oxidation (within the time period required for the experiment to be performed) and ultrahigh vacuum compatible. The main problem was that the tungsten filaments or thoriated tungsten filaments were strongly affected by the presence of oxygen in the residual atmosphere. In the first place we had to find filaments capable of emission of at least $50 \mu A$ at relatively low filament temperatures (800K) and select those which would not affect UHV and at the same time would be stable with respect to oxidation. During the experiments it appeared that the filament design affected also the emission stability of the diode. Till now we have tested clean Ni and W filaments, thoriated W, several mixtures of Ba, Sr, Ca, carbonates on W or Ni core, all of several different designs (e.g.: "needle", spiral, double and triple spirals, several thickness of the wires etc.). We may conclude that all carbonated filaments examined do not fullfil the requirements of our

experiments because of the oxygen production during operation, and relatively high operational temperatures. The filament design and preparation was carried out with the help of Development department of the local electric bulb factory. A simplified picture of the diode probe unit and its position on the apparatus is given in ref.1.

c) Thermal desorption spectroscopy.

All the relevant technical details and scientific performances are given in ref.1 (see enclosures).

The only difference between the present situation and that given in ref.1 is that the ion pump has been replaced by 170 l/s Balers Turbo pumping unit.

4. Results

The main experimental activity was focused on the experiments utilizing thermal desorption spectroscopy to study the interaction of oxygen with polycrystalline palladium foils. The time consuming step in this kind of experiments is the cleaning of the sample. We have tried several procedures described in literature, but eventually we found out some modifications which enabled us to obtain atomically clean surface of palladium foil. The sample has been sputtered by 3keV Ar⁺ beam (5-8 μ A) for several hours at sample temperature of 1200K. After quick annealing to 1350K, the sample temperature was reduced to 920K and sample exposed to $1 \cdot 10^{-7}$ Torr O₂ for several hours, followed by quick flash to 1350K in order to remove in-surface and sub-surface oxides. The cleaning proceeds by a series of 10L O₂ exposures and thermal desorption flashes with mass spectrometer tuned to mass 28 (CO-carbon monoxide) or 32 (O₂). When 28 signal was absent we tried for 32 signal. When there was no 32 signal we repeated the whole procedure from the beginning.

We have performed a number of experiments of oxygen adsorption/desorption on/from palladium surface, keeping the latter at various temperatures: 100K, 270K, 400K, 525K, 650K and 775K. We observed three groups of peaks in our spectra: i) low temperature signals in the range of 120K-220K Fig.1, ii) high temperature signals in the range of 580K-1050K, Fig.2 and Fig.3, and iii) a signal appearing at 1300K.

The first group (Fig.1) is ascribed to the molecularly adsorbed oxygen. In order to observe these signals one should keep palladium foil at 100K during oxygen adsorption. It is not quite clear whether dissociative adsorption also takes place at this temperature or dissociation occurs during the heating of the sample. However, we observe both groups of signals (i) and (ii), the former being the dominant one, at least for moderate coverages. There is a strong competition for the available surface sites between O_2 and carbon monoxide (CO) molecules. CO chemisorbs on the palladium surface while O_2 physisorbs, leading to a situation in which CO replaces O_2 very efficiently. In general, this and similar roles of CO in chemical reactions, adsorption and coadsorption problems have given rise to a large interest in CO-metal surface interactions, some of which we have also studied theoretically (refs.3 and 4). This interest is put to the fore by the role the CO molecules play in corrosion problems and related phenomena. In order to avoid problems with CO coadsorption we have performed the majority of our measurements at 525K, which is above the CO desorption temperature. Some typical spectra are shown in Figs.2 and 3. We could not reach the saturation of these signals, although we made exposures of several thousand Langmuirs. This is possibly a consequence of very low sticking coefficient for oxygen at higher coverages and the existence of CO and H_2 in the residual atmosphere. Both, H_2 and CO could be oxidized, giving water and CO_2 , thus taking away the oxygen atoms from the palladium surface. Here it should be noted that palladium is very well known catalyst in a number of chemical reactions. We ascribe these peaks to the chemisorbed oxygen atoms. There are two major points regarding their properties, behaviour and adsorption geometry position. For exposures up to 50L (Fig.2) there appear desorption peaks which shift to lower desorption temperatures, and this is characteristic of second order desorption. By careful and tedious analysis of these peaks^{5,6} we found that repulsive lateral interaction between oxygen atoms takes place and/or a continuum of surface site energies exists. As a result of these studies we developed a simple method for estimating the preexponential factors and lateral interactions which describe the thermal desorption spectra⁷. Fig.3 shows the spectra obtained for higher coverages. It is clear that a new peak appears with the increase of the coverage. Eventually, this peak dominates the whole high temperature spectrum. It shifts to higher desorption temperatures which

is characteristic of attractive lateral interactions. However, it would be beyond the scope of this report to discuss all our results in more detail. This will be done in a separate publication to be submitted to an open scientific journal. The third group of peaks appears at 1300K. These are due to the desorption of subsurface oxygen. We have never been able to observe the entire peak because it was always very broad and its higher temperature end lied beyond the limit given by the physical properties of the sample spotwelded to tungsten wires.

References:

1. M.Milun, P.Pervan, B.Gumhalter and K.Wandelt
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8. M.Milun, P.Pervan and K.Wandelt, in preparation.

Fig. 1

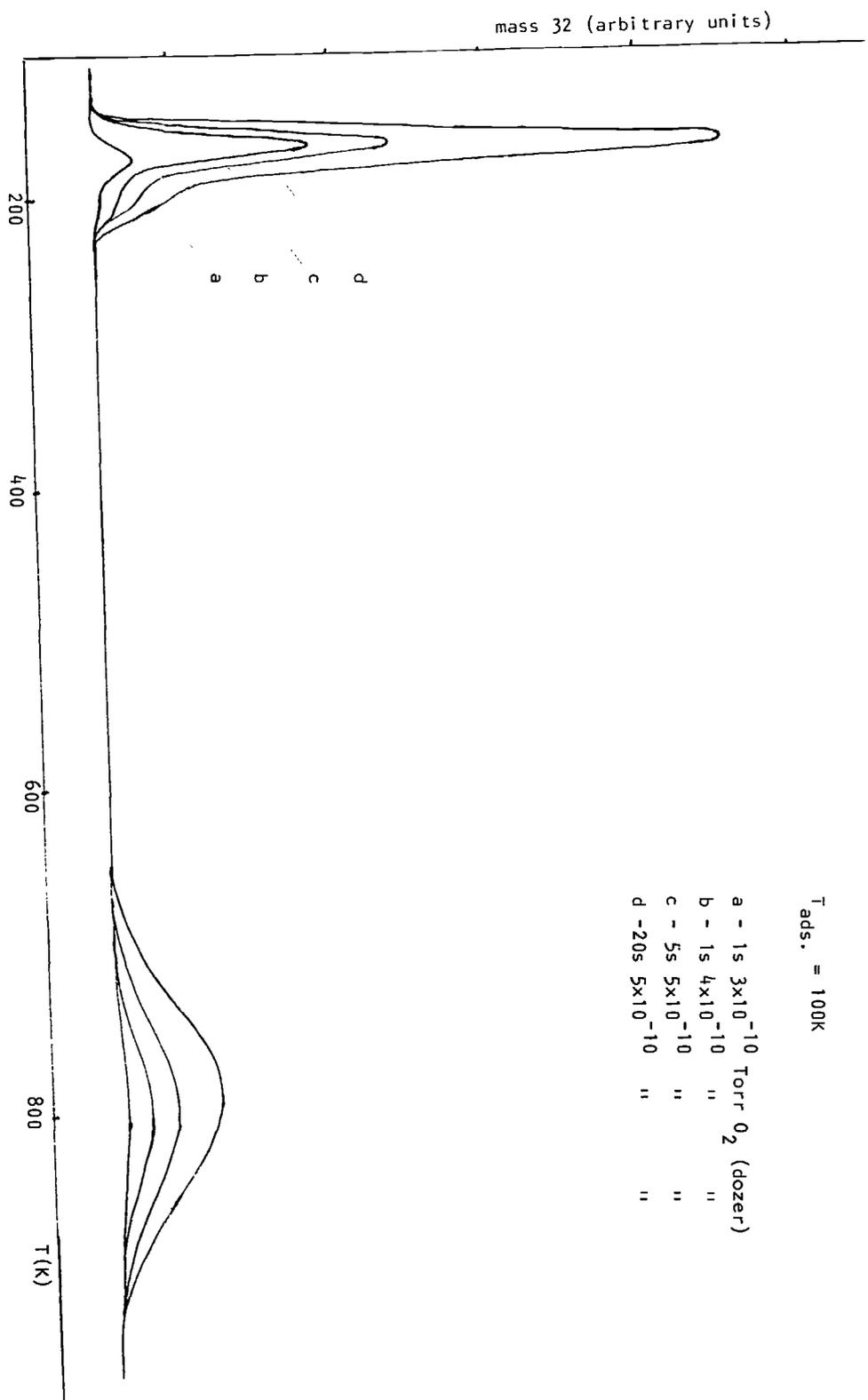


Fig. 2

Desorption rate curves of O_2 from polycrystalline Pd foil for different exposures of O_2 (a-g), performed at 300K. The heating rate β was $10Ks^{-1}$.

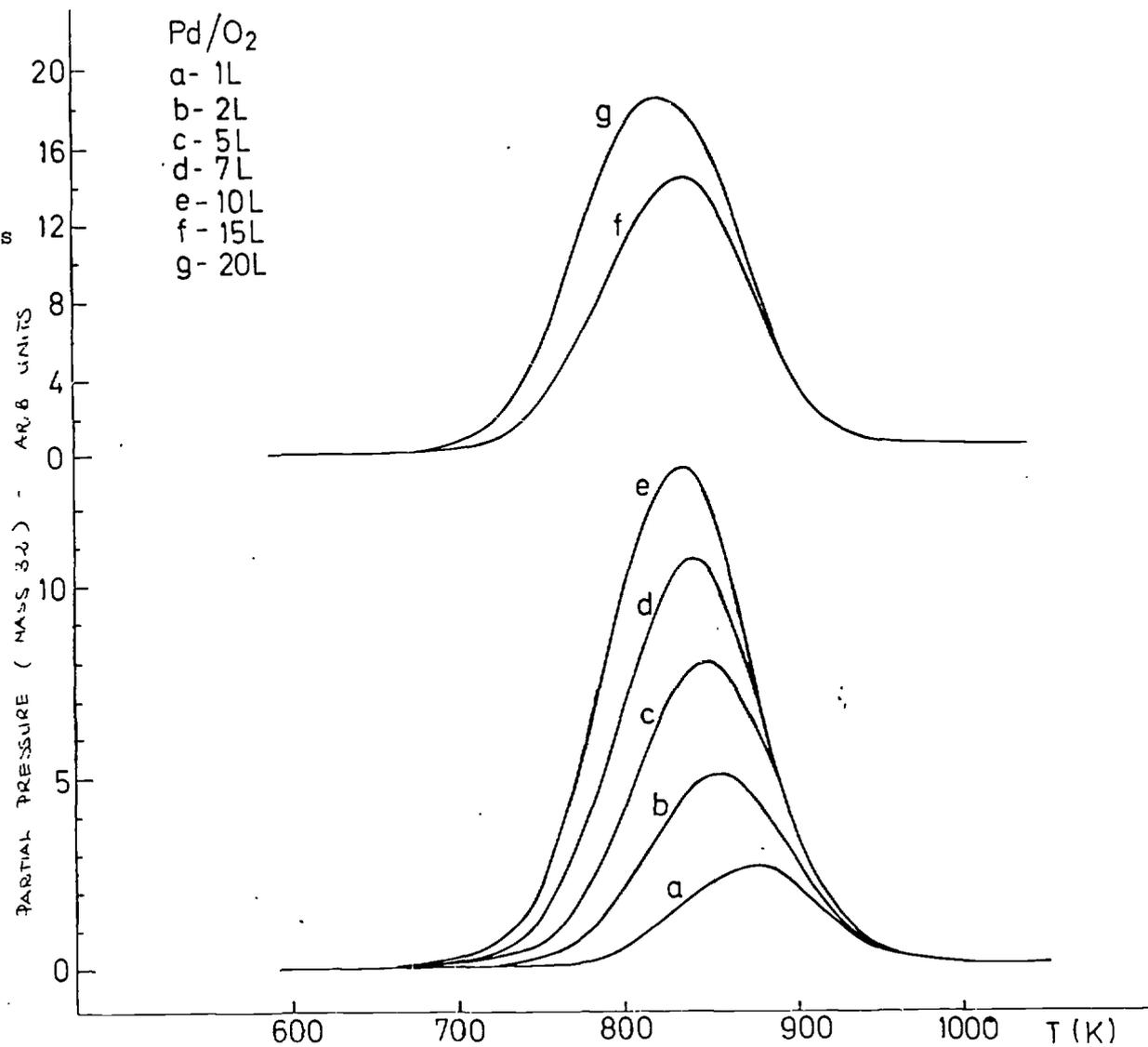
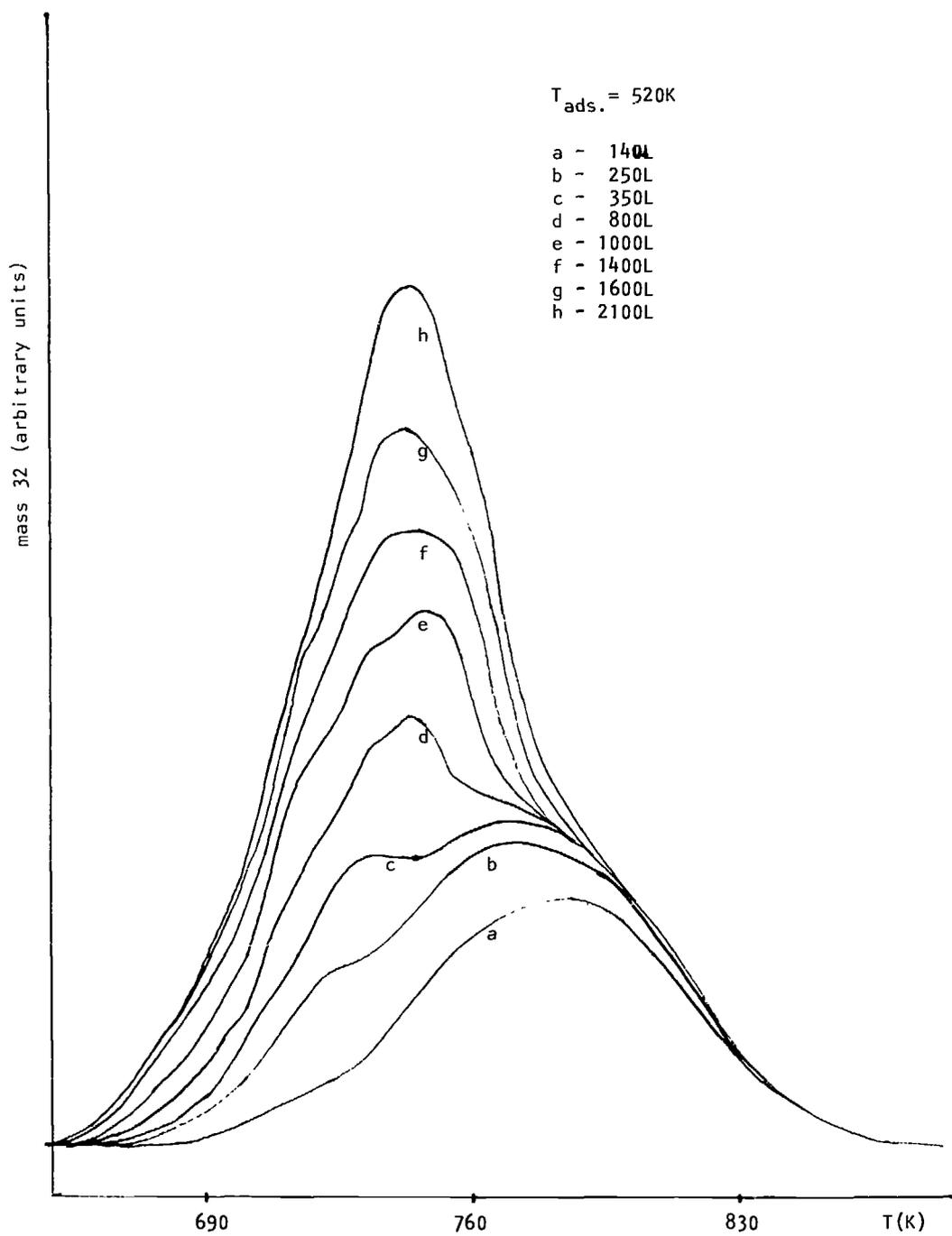


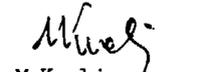
FIG. 3



6. Project expenditures (\$)

Project	Total	Personnel	Expendable sup.	Agency
RC 3227/R3	44.000	29.000	9.500	5.500
RC 3227/R2	43.500	28.200	9.300	6.000
RC 3227/R1	46.050	28.200	9.350	8.500
RC 3227/RB	36.495	27.495	3.000	6.000
	170.045	112.895	31.150	26.000


Dr. B. G. Galt,
Principal Investigator


M. Kralj
Chief Accountant

S U M M A R Y

RC 3227: "Development of a nondestructive testing method and facility for investigation of surface reactions appearing in damage, corrosion, adsorption, absorption and catalytic processes encountered in the heat transfer systems of nuclear power plants and in the energy storage problems".

Research Institution: Institute of Physics of the University Zagreb,
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Principal Investigator: Dr.B.Gumhalter

Period of Contract: 1.8.1982. - 31.7.1986.

In order to approach numerous problems connected with occurrence of corrosion, oxide layer growth, contamination etc., one has to study physical and chemical properties of surfaces of the materials used for construction of tubing of Nuclear Power Plant heat exchangers. These studies necessitate the investigation of processes which take place only at surfaces: adsorption and desorption. In this context two problems are of major importance: i) initial stages of oxidative attack e.g. the adsorptive properties of oxygen for a given system and possible synergetic effects of coadsorbed species like CO , H_2O , OH , H_2 , SH_2 , impurities, and ii) the influence of surface conditions (crystallography, defects, pores, impurities, segregates) on the oxidative attack. Within the project, we have developed an apparatus with three surface sensitive techniques: a) quartzcrystal microbalance as a method for measuring the kinetics of deposition of thin metal films and gas adsorption, b) diode probe for the measurement of work function change caused by gas adsorption at metallic surfaces, and c) thermal desorption spectroscopy (TDS) which gives information on adsorption/desorption properties of a system studied: activation energy, preexponential factors for desorption, coverage, precursor states, lateral interaction etc.

The system investigated was oxygen/palladium foil (polycrystalline). It was studied by means of TDS and the following conclusions have been drawn: 1. Oxygen adsorbs on Pd foil both dissociatively and

nondissociatively - depending on the adsorption temperature. 2. Certain amount of oxygen penetrates into the surface and subsurface region, giving rise to a desorption peak around 1350K. 3. There are two groups of desorption peaks corresponding to atomically adsorbed oxygen (730 K and 800 K). The analysis of these peaks show the existence of strong lateral interactions between oxygen atoms at high coverages, which is not the case for low coverages. The position of the peaks and the dynamics of their evolution is consistent with the data obtained for Pd(111) and Pd(100) single crystal surfaces.

- Papers: 1) M.Milun, P.Pervan, B.Gumhalter and K.Wandelt, Fizika 17
(1985)49
- 2) B.Gumhalter, Phys.Rev.B33(1986)5245
- 3) B.Gumhalter, Surf.Sci.157(1985)L355
- 4) P.Pervan and M.Milun, Fizika 18(1986)47