THE DEUTERIUM INTERACTION WITH TUNGSTEN AND IRIDIUM IN THE UHV SYSTEM

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The behaviour of hydrogen, in its contact with the iridium and the tungsten filament kept at different temperatures, was studied in the pressure range $1\cdot3 \,.\, 10^{-6}-1\cdot3 \,.\, 10^{-3}$ Pa, in a glass apparatus. The effects of adsorption, atomization, desorption, recombination of atoms and chemical reactions were investigated as a function of temperature of the filaments. The named individual processes were used for interpretation of the partial pressure changes in the apparatus. The significance of the above individual phenomena in the UHV experiments is pointed out in this paper.

The investigation of the behaviour of hydrogen, in its contact with the metals, is of practical importance in the vacuum technology. Hydrogen always constitutes a major part of the residual gases in the ultra high vacuum instruments. During the performance of these instruments, hydrogen gets into contact with the hot metal filaments, applied as cathodes in the vacuummeters, ion sources, electron guns *etc.* Likewise, in the low pressure catalytic and adsorption interactions of hydrogen, we meet cases where the results may be undesirably affected by the contact of hydrogen with the parts of the measuring instrument (*e.g.* mass spectrometer, vacuummeter). The observed distorsion of data is therefore the consequence of the specificity of work under high vacuum conditions, at which the reactivity of the surfaces plays a dominant role. The reactivity of the surfaces is thus responsible for the characteristic properties of each apparatus, given by the geometrical arrangement of the components, selection of the constructional materials, history of the preceding measurements and finally, by the choice of the studied system. The observed uniqueness of each apparatus is, nonetheless, a sum of individual interactions and processes proceeding any time when the used materials get into contact under comparable conditions. These individual processes are independent of the particular apparatus and thus they represent a common feature. In the present paper, we have investigated from the above point of view the deuterium interaction with the iridium and the tungsten filament, with special regard to the extent in which this interaction is affected by the presence of the glass walls in the apparatus. For technical reasons (purity of gas), deuterium was used instead of hydrogen. There is no reason why the isotopic effect should change the qualitative conclusions of this paper.

EXPERIMENTAL

All measurements were carried out in an all glass apparatus (2 400 cc), equipped with a reaction vessel with the iridium and the tungsten filament, an omegatron gauge, a freezing finger and a glass valve (Fig. 1). An oil diffusion pump filled with Convalex oil and an ion pump were used for pumping. Both pumps were separated from the measured volume by bakeable valves. After an 8-hour baking of the apparatus at 670 K (including the ion pump), the apparatus was left to cool down overnight, using uninterrupted pumping with the diffusion pump. Both metal filaments of the omegatron and the vacuummeter were then degassed for 3 hours under permanent pumping with both pumps. At this point, the apparatus was ready for the measurement. The final pressure reached at this stage was $2 \cdot 7 \cdot 10^{-7}$ Pa. The filaments of the studied metals were 22 cm long and 0·1 mm in diameter, with tungsten, and 18 cm long and 0·2 mm in diameter, with iridium. Deuterium (Technische Gase Leipzig, puriss.) was cooled down with liquid nitrogen before each experiment, in order to remove the condensable species (especially water). The operation pressure of deuterium in the apparatus ranged from $1 \cdot 3 \cdot 10^{-6}$ to $1 \cdot 3 \cdot 10^{-3}$ Pa. Both filaments were heated during the reaction at different temperatures. The heating voltage at the filaments was applied either in one step or it was changed according to a time dependent program. The programmed change of temperature was carried out in three steps: a gradual temperature increase, a period of constant maximum input and finally a gradual temperature decrease. Two rates of the change of voltage were used for each metal: 0·3 V/s and 0·13 V/s for tungsten and 0·14 V/s and 0·06 V/s for iridium. The rates for the upwards and downwards changes were identical. The duration of the constant maximum input was varied.

The apparatus used was a modified arrangement previously applied for autoemission microscopy. The arrangement was thus not optimal for the quantitative evaluation of the temperature desorption spectra, *e.g.* for the calculation of the activation energies of desorption. The obtained curves permitted to draw only qualitative conclusions[1].
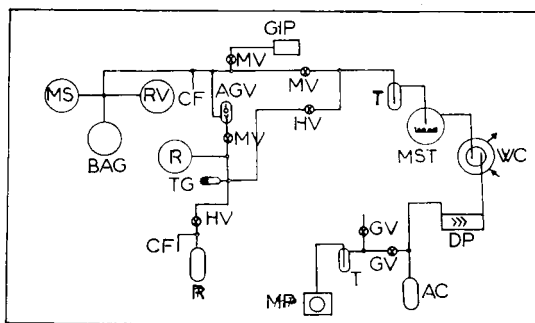

Fig. 1

Scheme of the apparatus. MS: mass spectrometer, BAG: Bayard–Alpert manometer, RV: reaction vessel, CF: freezing finger, R: reservoir D_2, GIP: ion pump, AGV: ground glass valve, MV: metal valve, TG: thermocouple manometer, HV: Hoke valve, T: trap cooled with liquid nitrogen, AC: sorption pump with active carbon, MST: vapour trap with molecular sieve, WC: water cooled vapour trap, DP: diffusion pump, GV: greased valve, MP: mechanical pump

RESULTS AND DISCUSSION

The courses of the programmed heating of individual filaments are shown for several typical conditions in Figs 2—5. Each course corresponds to a sequence of several subsequent processes; *a*) the desorption of hydrogen *b*) decomposition of water *c*) atomization of hydrogen and emission of the atoms towards the glass wall *d*) recombination of the hydrogen atoms *e*) adsorption of hydrogen. The desorption of hydrogen appears with both metals as a sharp maximum at the onset of heating. The water presence in the apparatus causes a broadening of the above desorption peak. This effect is much more visible with tungsten where water is bound more strongly (Fig. 3), than with iridium where the peak is only rounded-off, close to the maximum (Fig. 2). The peak broadening is connected with the formation of hydrogen during the water vapour decomposition, which becomes increasingly significant with the temperature rising during the desorption and after it. Besides hydrogen, carbon monoxide and carbon dioxide were also detected as additional products
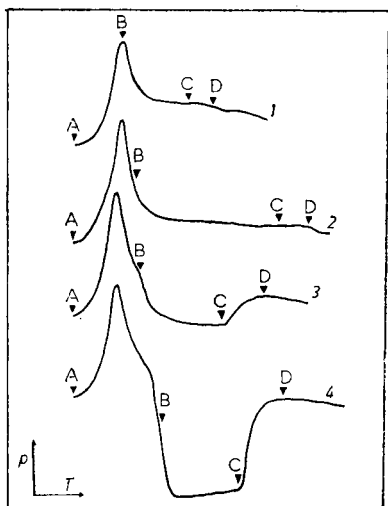

FIG. 2

Course of the hydrogen signal during the programmed heating of the iridium filament, in hydrogen, with addition of the water vapour ($p_{tot} = 5{\cdot}5 \,.\, 10^{-4}$ Pa); A—B: rising temperature, B—C: interval of constant maximum temperature, C—D: decreasing temperature; temperature of the region B—C: *1* 960 K, *2* 1 070 K, *3* 1 250 K, *4* 1 320 K
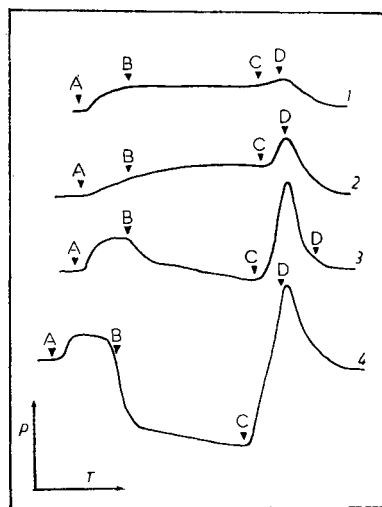
FIG. 3

Course of the hydrogen signal during the programmed heating of the tungsten filament, in hydrogen, with addition of the water vapour ($p_{tot} = 9{\cdot}0 \,.\, 10^{-4}$ Pa); A—B—C—D: see Fig. 2; temperature of the region B—C: *1* 1 300 K, *2* 1 340 K, *3* 1 470 K, *4* 1 620 K

of the water decomposition, formed by the reaction of carbon at the metal filaments. In literature we can also find described the formation of the metal oxides in the course of the water decomposition at tungsten[2]. This result is supported also by the fact that no molecular oxygen was detected at both filaments. The overall temperature range within which water is decomposed cannot be determined from the hydrogen signal, since this process is overlapped by the competing processes of hydrogen atomization and adsorption of the formed atoms at the walls of the apparatus. While the water decomposition leads to an increase of the hydrogen signal, atomization of hydrogen results in its diminution. The competition of both processes can be clearly seen when the maximum temperature of the heated filaments is gradually increased during the programmed heating (Figs 2 − 3). The interpretation is, however, complicated by the fact that the threshold temperature of the hydrogen atom formation in the water vapour decomposition at both metals is not known. This temperature is not identical with the threshold temperature of atomization of the molecular hydrogen. At sufficiently high temperature of the filament, the atomization process
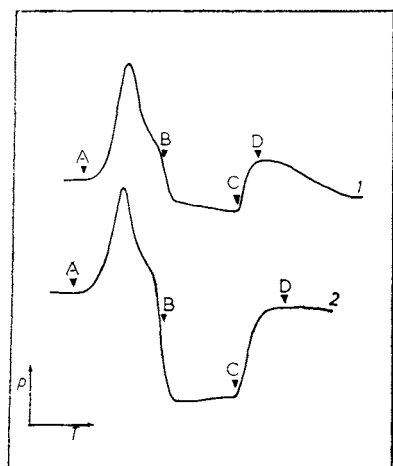

FIG. 4

Course of the hydrogen signal during the programmed heating of the iridium filament, in hydrogen, dried by a freeze-out with liquid nitrogen ($p_{tot} = 7{\cdot}5 \,.\, 10^{-4}$ Pa, maximum temperature of the iridium filament 1 320 K); *1* with simultaneous heating of the tungsten filament at 1 570 K, *2* tungsten filament at room temperature, A−B−C−D: see Fig. 2
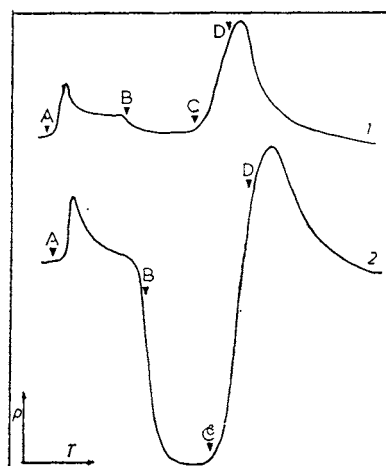
FIG. 5

Course of the hydrogen signal during the programmed heating of the tungsten filament, in hydrogen, dried by a freeze-out with liquid nitrogen ($p_{tot} = 5{\cdot}0 \,.\, 10^{-4}$ Pa, maximum temperature of the tungsten filament 1 600 K); *1* with simultaneous heating of the iridium filament at 1 470 K, *2* iridium filament at room temperature, A−B−C−D: see Fig. 2

becomes so predominant that it decreases the hydrogen signal level below its stationary value, so that we find at the signal curve a drop, followed with a flat bottom. If this depression is maintained by prolonged duration of the maximum power input, the amount of hydrogen removed from the gas phase increases and, consequently, the glass wall coverage of the reaction vessel with hydrogen atoms goes up. The recombination rate at the glass wall hence also rises and under the conditions of permanent hydrogen injection at the filament, and with a constant heating rate, the depth of the depression decreases with time. As the recombination at the walls proceeds under uninterrupted bombardement with the hydrogen atoms, the mechanism of the atom addition from the gas phase, onto the adsorbed atom, is evidently dominant. According to Hickmott[3], this process is much faster than the recombination process which proceeds only between the atoms at the walls.

The course of the hydrogen signals, in the region of the depression, is quite different when the second filament is simultaneously heated at constant temperature. The depth of the drop, under such circumstances, is always smaller; the higher is the temperature of the steadily heated filament (which is in all cases switched-on before the start of the programmed heating), the smaller is the depth of the depression (Figs 4 – 5). The magnitude of the drop is also smaller in the case when the constant heating of the second filament is applied first and then switched-off just before the commencement of the programmed heating.

According to both observations, the above supression of the hydrogen partial pressure depression (observed when the second filament is heated at constant temperature) can be explained by increased atom recombination at the glass walls. The increased atom recombination is related to the higher hydrogen atom surface concentrations arising from the performance of the constantly heated filament. The pressure drop resulting from the atomization at the filament with the programmed heating is then smaller or it diminishes at all.

An interesting phenomenon of the programmed heating at the tungsten filament is a pressure maximum observed during the filament cooling (Fig. 5). (We shall refer further to this peak as "a peak of cooling".) The above effect resembles evidently the pressure increase observed after switching off the filament, by Peterman and Baker on molybdenum[4] and by Murakami on rhenium[5]. The increase of the hydrogen partial pressure above its stationary value must be caused by liberation of the hydrogen from some additional source. Such source can arise either from the decomposition of water or from a hydrogen reserve, formed in the system during the filament heating, which is released into the gas phase after switching off the filament. Since we have found no marked difference in the form and magnitude of the peak of cooling, between the cooled-down and non-cooled hydrogen, the pressure increase during the cooling cannot be attributed to the water decomposition, since this rate depends on the partial pressure of the initial compound which is in the two cases different. The pressure increase must therefore originate from

a supply of hydrogen in the form of the hydrogen atoms adsorbed at the glass wall. In accordance with that, the peak of cooling is observed only in such a case when the temperature of the tungsten filament, at its maximum input, exceeds 1 200 K (which is the threshold temperature of the hydrogen atomization[6] needed for the formation of the hydrogen reserve). The supply of hydrogen in the region of the peak of cooling can be exhausted only by some kind of a recombination process. If the pressure rose as the result of recombination of the atoms at the glass surface, it would be difficult to explain why this increase takes place exactly during the period of the filament cooling, when the emission of the hydrogen atoms from the metal surface practically drops to zero. Consequently, there stops also the fast recombination process of the atom addition from the gas phase, onto the atom adsorbed at the glass wall. We can localize the source of the peak of cooling when we operate the tungsten filament under conditions of the programmed cooling, while the heating of the iridium filament is kept at constant temperature. It is also necessary to lower the water vapour pressure in the hydrogen by a freeze-out. If the iridium filament is kept at sufficiently high temperature, no signal drop is observed. Hence, it is evident that the tungsten filament cannot serve as the hydrogen reservoir. Nonetheless, during the cooling of the tungsten filament, we again find the cooling peak, in spite of the fact that the iridium filament is kept glowing at constant temperature. Since during such experimental conditions, the recombination process at the glass walls becomes slower, we can consider only the recombination in the gas phase and at the filaments. Both possibilities inherently assume that the pressure of the hydrogen atoms in the glass volume has a non-zero value. We can omit the recombination in the gas phase because of the low pressure and the mechanism. The extent of the exothermic recombination at the filaments goes down with the rising temperature. During the above described experiment, the iridium filament is glowing and the rate of recombination on it is therefore low and constant. The tungsten filament, on the other hand, cools down and under otherwise unchanged conditions its recombination capacity goes up. This leads to an increase of the hydrogen partial pressure, up to the maximum of the peak of cooling.

So far we have considered the rising part of the peak of cooling. The subsequent decrease from the maximum down to its stationary value, can be assigned to the consumption of the hydrogen reserve. Nevertheless, the peak of cooling appears also when the iridium filament is simultaneously kept at the constant temperature of atomization, *i.e.* under conditions where the above mentioned reserve is permanently restored. For the origin of the descending part of the peak of cooling, we must therefore look back at the surface of the tungsten filament. This surface is after the heating rather clean so that in can catalyze the recombination of the atoms. During the cooling, the surface is gradually covered with water or other occasional contaminants, so that its surface recombination activity diminishes and the partial pressure of hydrogen goes down. The peak of cooling is therefore formed by pumping

of the atoms from the glass wall, over the gas phase, to their subsequent recombination at the cooling-down tungsten filament. This process proceeds up to the moment when the surface is desactivated by the adsorbed species.

The assumption that the recombination process proceeds at the tungsten filament can be experimentally supported by deliberate poisoning of the tungsten surface. If the filament is in advance nitrided by heating at 2 400 K, in nitrogen at 5 Pa, no peak of cooling in hydrogen is observed. When nitrogen from the surface is removed by longer vacuum heating, the filament regains its recombination activity and the peak of cooling again is observed.

If the above concept is valid, then the peak of cooling must depend on a suitable course of the filament cooling. Under conditions of slow cooling, part of the hydrogen atoms which are pumped from the glass walls into the gas phase, returns back from the still hot filament onto the glass wall, in an unchanged atomic form. Consequently, the overall recombination rate at the filament becomes slower and the peak of cooling is broadened, if it does not disappear at all. The peak of cooling becomes for the same reason smaller when the programmed heating of the tungsten filament is terminated above the room temperature (Fig. 6). Complete disappearance of the peak is observed
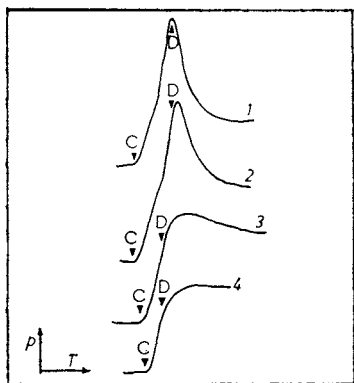

FIG. 6

The effect of the final temperature of the programmed heating of the tungsten filament, at the course of the peak of cooling ($p_{tot} = 7 \cdot 10^{-4}$ Pa); C commencement of the temperature decrease, D termination at the final temperature; final temperature: 1 293, 2 520, 3 1 130, 4 1 250 K
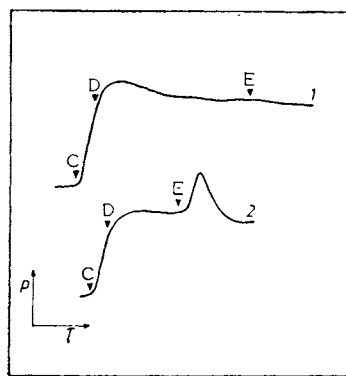
FIG. 7

The effect of the final temperature of the programmed heating at the tungsten filament, at the course of the hydrogen signal, after switching off the input power ($p_{tot} = 7 \cdot 10^{-4}$ Pa); C commencement of the temperature decrease, D termination at the final temperature, E switching off the power input; temperature of the region D—E: 1 1 130, 2 1 250 K

only above the threshold temperature of atomization. If the temperature drops below this threshold after switching off the heating, the peak of cooling is again observed (Fig. 7). We have never observed under comparable conditions the peak of cooling with the iridium filament. One of the reasons can be again connected with the course of the filament cooling. If the main proportion of heat is carried away by the connector wires, then the used iridium wire cools down more slowly than the tungsten wire, since with equal specific heats, the iridium wire has lower heat conductivity and a larger mass.

It has been already mentioned that water in the apparatus can interfere with the hydrogen reactions, unless its tension is decreased by a freeze-out. The course of the partial pressure of water during the heating of the tungsten and the iridium filament resembles in major the similar curves of the partial pressure of hydrogen, though for different reasons. At the beginning of the heating, water is desorbed from the filament and as a result, we observe on the signal curve a peak. This peak is followed by a drop which is due to the water decomposition at the hot filament. The bottom of this depression gradually rises with prolonged heating. We attribute this fact to the increasing water desorption from the glass walls, which are more and more heated by the radiation from the filament. If the heating of the filament is stopped abruptly, we can even see the peak of cooling of water. This peak is not observed in the case of the programmed gradual heating. The formation of this peak can be explained by competition of the water desorption from the glass walls and the water decomposition at the hot filament. During the cooling of the filament, the glass wall cools as well, due to a decreased supply of radiated heat. Hence, both the decomposition of water and its desorption from the walls of the reaction vessel are slowed down. If we stop the filament heating instantaneously, the filament cools down quickly and the water decomposition is terminated sooner than the water desorption from the walls. In the case of the programmed cooling, the temperature of the filament decreases more slowly so that the water decomposition extends approximately over the whole period of desorption from the walls. Consequently, the peak of cooling is not observed. This peak is thus, basically, a record of the time dependence of the above-stationary water tension released from the walls.

CONCLUSIONS

The described effects sufficiently illustrate the variety of effects accompanying the apparently uncomplicated process of heating a filament at very low pressures of gases with simple structures. It is obvious that in the region of the high and ultrahigh vacuum, where the total amount of particles in the gas phase is relatively small, the material properties of the studied object and of the applied measuring device become important. The chemical properties of all surfaces which are in contact with the gas phase are influenced by the adsorption-desorption processes. On the

other hand, they are also affected by the transport phenomena in the solid phase which proceed between the volume and the surface in both directions and which are increasingly important at higher temperatures. This is important especially for the TDS method which became lately quite widespread[7,8]. The atoms migrating in the solid phase usually have small dimensions (*e.g.* hydrogen, nitrogen, carbon).These atoms are introduced into the material either during the technology procedure or as the consequence of reactive dissociation of the molecules from the gas phase during the measurement itself. Such splittings leading to the formation of gaseous atoms are a common feature in the operation of the vacuum gauges.

Due to the described factors, the chemical composition of the surfaces inside the apparatus is never constant and accordingly the influence of their surface area, which is usually much larger than the surface of the sample, can never be omitted. The composition of the surface is already changed during the measurement itself. However, due to the slowness of the transport in the solid phase, each series of measurements changes the material composition which is never renewed completely. In this way, the results of each experiment depend on the conditions at which the system was treated before. Each combination of the apparatus and the measured object thus becomes to certain extent unique and the obtained information cannot be uncritically transferred elsewhere. For the comparison of the results obtained not only with different apparatusses, but also in different series measured at the same apparatus, it is important to study primarily the composition of the gas phase.

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