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GAS RELEASE FROM MECHANICALLY AFFECTED METALS

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In addition to spontaneous outgassing of materials and desorption stimulated by particles or photon bombardment, the gas release from mechanically affected materials was recently discovered as another source of gas in vacuum systems. Particularly, outgassing due to operations of manipulators and transmissions becomes a limitation in attaining low pressure in UHV systems used for production of semiconductor devices (e.g. MBE systems). Experiments are reported that were carried out to study gas release from metals when samples of metals were mechanically affected by rubbing the sample surface by another body or by deformation of the sample. Results of the experiments lead to the conclusion that gases dissolved in the metals and diffusing out when the sample is mechanically affected, represent the main source of the released gases. Adsorbed gases are released by mechanical treatment, too, but in much smaller amount. Mass spectroscopic analysis showed that tribochemical reactions among released gases, residual gases and material of the sample took place on the rubbed surface providing new gases into vacuum.

1. *Introduction*

It was observed that outgassing occured in vacuum system during action of mechanical devices that consist of movable or deformable parts. Opening and closing valve, movements of manipulators and motion feedthroughs, etc. cause steep rise of the pressure. More sophisticated equipment for production of semiconductor devices, e.g. the molecular beam epitaxy systems, contains many manipulators and transmissions enabling manipulation of products. Since outgassing due to operations of mechanical systems can disturb UHV conditions [1], the gas release caused by mechanical treatment of material draws much attention.

Mechanically stimulated outgassing can also change frictional properties of surface of a solid and its wear. The presence of very small amounts of foreign matter on a surface results in changes of its frictional behaviour. A thin layer of saturated hydrocarbons is often used as a lubricant, but also an adsorbed layer of gas molecules reduces friction [2]. The lubrication effect of adsorbed molecules is very strong and concentration of the adsorbed layer, which is only a fraction of a monolayer concentration, can substantially reduce the coefficient of friction [3]. It can be expected that an increase of the wear of the surface and of the friction coefficient will be observed after a surface is rubbed under vacuum, for rubbing of the surface reduces the concentration of the adsorbed layer. Increased damage to the surface was observed [4] when sample was rubbed under vacuum.

Only a few reports about this phenomenon have so far appeared. Simple modes of the mechanical actions causing outgassing of materials were studied: rolling a cylinder over a surface [5], rubbing the surface by another body [4,6], rotating a milling cutter in a conical hole [7], hitting a surface by a rod [6] and deformation of a tube by torsion [8]. This paper gives a brief outline of recent experimental results and summarises some ideas about processes suggested to explain mechanically stimulated outgassing.

2. *Experiments*

To reach the sufficient sensitivity of the outgassing measurements, the experiments were carried out in UHV conditions. In a vacuum chamber, a device was installed providing a desired mechanical action, and pressure changes were measured while a metal sample was mechanically affected. Several devices were used to perform various types of mechanical action: rubbing the sample with another body, hitting another body onto the sample surface or deformation of the sample. A gas-handling system was connected to the vacuum chamber through a variable leak-valve allowing exposure of the sample surface to various gases both before and during the mechanical treatment of the sample.

The experimental samples were prepared in various ways, differing in mechanical and thermal pretreatment, etching and grinding processes, cleaning procedures etc.

A sample was placed in the experimental set-up and after proper conditions were reached in the vacuum chamber, it underwent a mechanical treatment. The pressure in the vacuum chamber was measured by a Bayard-Alpert ion gauge. Composition of the gases released from the samples was measured by a quadrupole mass-spectrometer that allowed recording of up to 12 mass numbers simultaneously.

3. *Outgassing due to deformation*

Although a few experimental devices were built to measure outgassing of metals due to deformation differing in the shape of deformed body (bellows, sheet, tube), most of the relevant results were obtained with the device shown in Fig. 1 [8]. It consists of a metal tube, one end of which was connected to the vacuum system and the other one was closed. The closed end of tube was rotated by a torque wrench, so the applied moment of forces could be determined easily. The angle of rotation was measured by a variable resistor. The slider of the resistor was fastened to the revolving end of the tube. A heater was put over the tube to maintain the temperature at a required level.

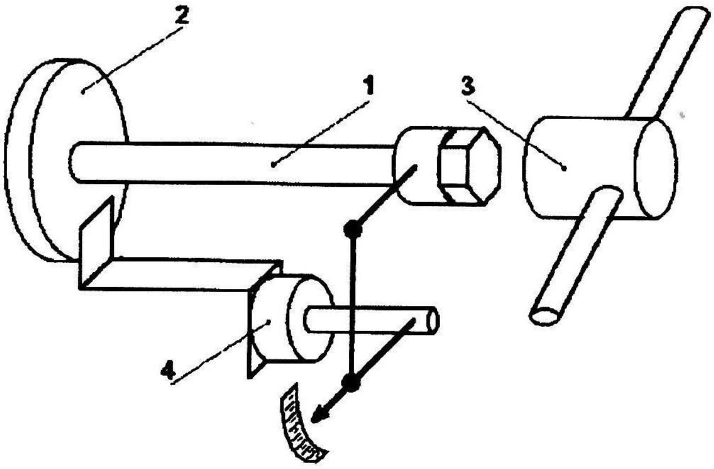
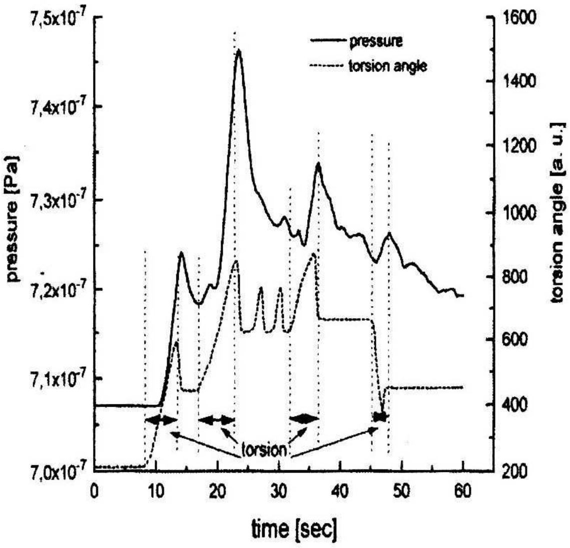


Fig. 1: Experimental device for the measurement of gas release due to deformation: (1) experimetal tube, (2) ConFlat flange, (3) torque wrench, (4) variable resistor.

The following results are typical examples of metal outgassing during deformation. They were obtained for a tube made of 304 type stainless steel and of dimensions: the length of 100 mm, the outer diameter of 10 mm and the thickness of wall of 1 mm. Time-pressure curves that were recorded, while the tube was twisted at base pressure of the vacuum system and the room temperature, are shown in Fig. 2.

No measurable gas release was observed until the moment of forces that twisted the tube exceeded a certain value (approximately 20 Nm for the tube used). Below the limit, the angle of twisting was proportional to the moment of twisting forces and the tube restored to the initial position after it was loosened. If the applied moment of forces was raised above this value, the tube did not stop twisting at a certain angle but it continued to twist around until the moment of forces was reduced or the tube was damaged. After the tube was loosened it didn't return to the initial position but remained deformed. A moment of forces had to be applied to the tube in the opposite direction to return the tube to the original shape. A gas release was observed during the time when the applied moment of forces exceeded the value that caused irreversible deformation. When the tube was repeatedly twisted backwards and forwards, within the extent of the first deformation, the amount of released gas was reduced quickly and after several cycles it became unmeasurably small. Another quantity of gas could be released by increasing the twisting angle. The gas release that vanished after the tube was twisted several times, both forwards and backwards, was also renewed when the tube was heated to approximately 200 °C for 1 hour and then cooled down.



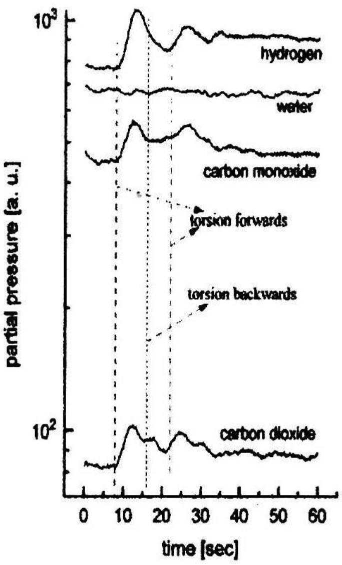


Fig. 2: Variation of total pressure and torsion angle during deformation of a tube.

Fig. 3. Variation of partial pressure during deformation of a tube (right).

Changes of the partial pressures of some gases are shown in Fig. 3. Hydrogen is the main component of the released gas. Also, a small amount of carbon monoxide and dioxide was found to be released, but in contrast to the hydrogen, these gases did not seem exhausted during repeated deformation.

4. *Outgassing due to rubbing*

After a long series of experiments, a device for the measurement of outgassing due to rubbing in well defined and controlled conditions was developed as it was previously reported in more detail [7]. It consists of a tool in the shape of a conic milling cutter covered by a layer of TiN that rotated within the hollow sample. The tool was supported by needle bearings and the transfer of motion was performed by means of a magnetic field. During an experiment, the tool made several turns while the pressure was recorded. A time-pressure curve for a typical experimental cycle with a stainless steel sample at room temperature is shown in Fig. 4.

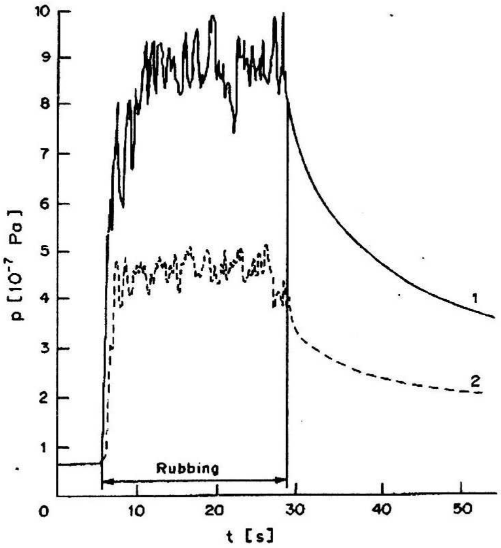


Fig. 4. Variation of total pressure during rotation of the milling cutter. Curve (1) during the 5th cycle, curve (2) after 100 cycles approximately.

To overcome some disadvantages of this arrangement (irregular movement of the tool on the sample due to magnetic transfer of motion, troublesome measurements at higher temperatures due to high heat capacity of the sample, difficulties with preparing of the samples due to their shape), another device was constructed that is schematically shown in Fig. 5. The whole system was designed as a nude one and its base was a ConFlat flange of 6 inch outer diameter. A sample holder was fastened to the flange with two stainless steel rods and samples in the shape of a thin rectangular plate were fixed to the upper surface of the holder. The tool was usually in the form of a cylinder made of thin metal foil, but tools of other shapes were used, too. The tool was attached to a stainless steel rod that was connected to the flange through bellows. The opposite end of the rod was joined to a driving mechanism that enabled the tool to do harmonical motion on the surface of the sample at various frictional contact loadings. An electric heater was placed inside the sample holder that allowed raising the temperature of the sample up to 900 K. As an example the time-pressure curves at two different contact loadings are shown in Fig. 6. They were measured during movement of a stainless steel tool on the surface of a stainless steel sample.

Both of these experimental devices were used to carry out a large number of measurements, some of them were described previously [4,7]. In most of the experiments, the sample and the tool were made of stainless steel, but gas release from nickel, aluminium, and OFHC copper was studied, too. An attempt was done to use the tool of “inert” hard material as silicone dioxide, titanium nitride, and saphire.

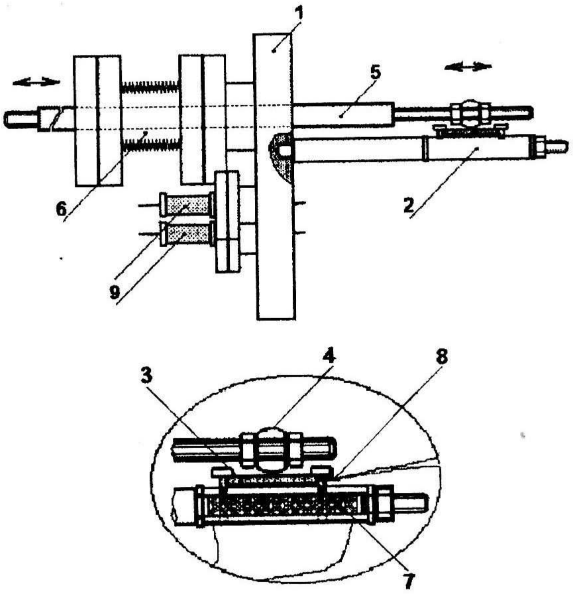
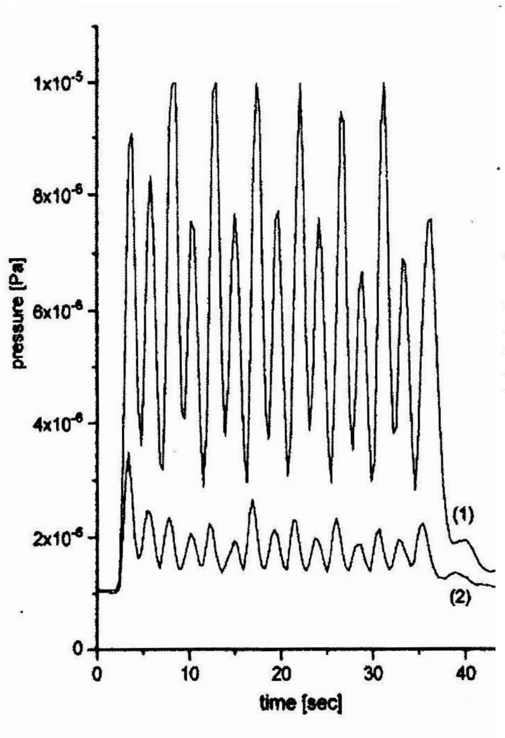


Fig. 5. Experimetal device for measurement of gas release due to rubbing of the surface: 1) 6 inch o.d. ConFlat flange, 2) sample holder 3) sample, 4) tool, 5) supporting rods, 6) bellows, 7) heater, 8) thermocouple, 9) feedthroughs to heater and thermocouple.

The experiments showed that measurable pressure pulses occured only when the force pushing the tool against the sample was strong enough to make microscopic craks and fissures on the sample surface. However, the surface was found to be torn after the sample was rubbed in the vacuum even if the contact force was smaller then 0.1 N per 1 cm length of the contact edge. The same treatment at atmospheric pressure left the sample surface without any damage.

The height of the pressure pulse due to rubbing diminished after each movement of the tool over the sample surface when a new sample was rubbed. The decrease became smaller when the rubbing continued and the height of the pressure pulse remained constant after approximately several tens of the movements. As the contact edge of the tool usually had an asymmetric shape, the heigths of the pressure pulses depended on the direction of the tool movement. The difference between the pressure pulses in the two directions diminished with increasing number of the movements of the tool. The rate of the decrease of the pressure pulse heigth was higher when the sample was outgassed by heating in vacuum before measurement.

The heigth of the pressure pulses could be restored by heating the sample to a higher temperature. Exposure of the sample to various gases at pressure up to 1 Pa for a few hours had no or only small effect.



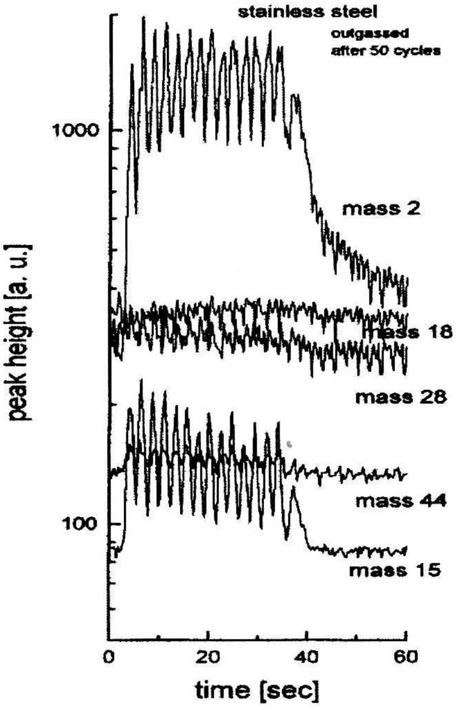


Fig. 6. Variation of total pressure during rubbing of the surface for various frictional contact loadings. Curve 1) was measured at higher pushing force then curve 2).

Fig. 7. Variation of partial pressure during rubbing of the surface (right).

The gas released during rubbing varied slightly in composition depending on the material of the sample and the tool. Figure 7 shows, as an example, the partial pressures of selected gases that were recorded in the vacuum chamber while a stainless steel sample was rubbed with a stainless steel tool. The main components of the released gas were hydrogen and methane, and a small increase of the partial pressure of water vapour, carbon monoxide, and carbon dioxide was observed, too. If the stainless steel sample and tool were outgased at a temperature above 1000 K in UHV before the measurement, the partial pressure of methane decreased in comparison to other components of released gas. The gases released from OFHC copper were mainly hydrogen, carbon dioxide, and methane, but water vapour, oxigen, and carbon monoxide were also observed. When the sample and/or the tool were made of nickel, besides an increase of the hydrogen and methane partial pressures, a decrease of the partial pressure of carbon monoxide was caused by rubbing.

Release of hydrogen, methane and carbon dioxide from all measured metals depended on the speed of the tool movement. On the other hand, partial pressures of some other gases (for example water vapour, carbon monoxide from stainless steel) increased during the rubbing slowly and were almost independent of the speed of the tool movement.

5. *Discussion and conclusions*

The results of the measurements of gas release due to deformation showed that gas release occured only when the plastic deformation had been reached and repeated deformations forwards and backwards without exceeding the extent of the first deformation did not cause release of another amount of gas. Heating at a higher temperature restored the gas release after it had vanished due to repeated deformations, but an exposure of the sample surface to the common gases (H_2, O_2, H_2O, CO, air) influenced neither the amount nor the course of gas release. The amount of the released gas due to deformation became larger as the temperature rose and the gases released from the stainless steel were those usually dissolved in it.

These findings allow us to conclude that the origin of the released gas is inside the bulk of deformed material. Most probably, the released gas is due to outgassing of dissolved molecules in the material.

Thermal outgassing due to the temperature rise caused by plastic deformation was suggested to be responsible for the observed gas release [6]. Heating of the deformed material due to plastic deformation was calculated and the temperature rise was found is too small to increase thermal outgassing sufficiently to explain our experimental results. Therefore, we consider displacement of the dissolved gas due to changes of a structure and a volume of the deformed material as a more probable cause of the gas release due to deformation.

Gas release caused by rubbing showed many aspects similar to those that characterized gas release due to deformation: the amount of the released gas decreased when rubbing was repeated, gas release could be restored by heating, the gases dissolved in the rubbed sample always appeared among the released gases and the rate of outgassing rose when the sample temperature was raised. From these results, one can conclude that plastic deformation played an important role in the process of gas release due to rubbing.

It is known [9] that during frictional proceses a continous boundary layer develops on the contact surface which has a disturbed lattice structure and changed composition in comparison to the bulk. In this layer, which is called the Beilby layer in tribology, futher processes appear, related to the plastic deformation and fracture processes. Plastic deformation of grains and lumps that occurs on friction could cause gas release in the same way as it was observed in the case of deformation of the whole sample due to twisting.

There are some aspects of gas release due to the rubbing that can not be related to the microplasticity in the contact Beilby layer. Appearance of a large amount of methane among the gases released from stainless steel during rubbing was considered as the most significant one, since any release of methane was not observed during deformation of stainless steel. Methane and some other gases that could not be supposed to be dissolved in the bulk were also released from nickel and copper during the rubbing.

As an explanation of the methane release, tribochemical reactions [9,10] were suggested. These reactions occur when interaction between rubbed surfaces is strong enough to create triboplasma [11,12] at points where surfaces are in touch. As triboplasma consist of highly excited energetic particles, which are characterized by the kinetic temperature above 10^4 K, the tribochemical reactions show a divergent kinetic and thermodynamic behaviour in comparison with thermally related reactions. Syntheses of methane and carbon monoxide are typical examples of the triboreactions.

Finally, the results of our experiments suggest that release of the gas adsorbed on the surface takes part in outgassing when the surface is affected mechanically. However, the amount of the desorbed gases is usually too small to be registered on the background of release of the gases dissolved in the bulk. Only if influence of the dissolved gases is avoided, the mechanically induced desorption becomes observable.

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ISPLINJAVANJE ZBOG MEHANIČKOG DJELOVANJA NA METALE

Pored isplinjavanja iz raznih materijala i desorpcije stimulirane česticama ili fotonima, nedavno je otkriveno isplinjavanje metala zbog mehaničkog djelovanja, koje je također izvor plinova u vakuumskim sustavima. Posebice, isplinjavanje zbog rada manipulatora i prijenosa uzrokuje ograničenje tlaka u ultravakuumskim sustavima. Proučavano je isplinjavanje iz površina metala zbog tarenja i zbog deformacija. Glavni uzrok otpuštanja plinova je izlaženje otopljenih plinova koji difundiraju kada se mehanički djeluje na metal. Adsorbirani se plinovi također otpuštaju, ali mnogo manje.