FEM STUDY OF OXIDIZED TUNGSTEN SURFACES

Jan ŠOTOLA[a], Vladimir SAVKIN[b] and Zlatko KNOR[a]

[a] *The J. Heyrovský Institute of Physical Chemistry and Electrochemistry,*
Czechoslovak Academy of Sciences, 182 23 Prague 8, Czechoslovakia
[b] *Institute of Chemical Physics,*
Russian Academy of Sciences, Moscow, Russia

Dedicated to Dr Miloš Kraus on the occasion of his 65th birthday.

Surface reconstruction of tungsten induced by oxygen chemisorption in the temperature range 300 K ≤ T ≤ 2 200 K, has been investigated by means of FEM. Two types of surfaces have been used in this study: (i) hemispherical tungsten tips exposing small low index planes and stepped regions to the gas phase; (ii) polyhedral tungsten tips exposing large densely populated planes. A model for the reconstruction of a (100) plane is presented, explaining all the phenomena observed by FEM, TDS, LEED and MBS.

Oxygen interaction with tungsten has been subject of numerous studies. In spite of that, some features of this process have still not been well understood. The oxidized tungsten surface has been used in our laboratory as a carrier for small metallic clusters (islands) simulating supported metal catalysts, where e.g. spillover effect in bimetallic systems can be investigated[1,2]. In a classical glass FEM available in this laboratory, only surface processes accompanied by work function changes (WFCs) can be investigated. We have focussed attention particulary onto qualitative results, i.e. on the change of sign of the WFCs (from increasing to lowering of the WF). Interpretation of such effects on metals can be based on simplified models. The increase and decrease of the WF are frequently attributed to the formation of a dipole layer having respectively, negative and positive charges on the vacuum side (Figs 1a – 1c). An alternative explanation[3] of the increased emission from a given area may be sought in surface reconstruction induced by chemisorption. Namely, microscopic roughening and smoothing of a particular region of the sample surface leads respectively to lowering and increasing of its work function as suggested by Smoluchowski model of the metal surface[4] (Fig. 1d). Additionally, the change of the macroscopic shape of the tip (creation of new edges and/or corners) influences distribution of the electric field in its vicinity. This might result in a different emission pattern of the tip. In the interpretation of the increased brightness of a certain region of the FEM image (increased emission of a particular region of the

sample surface in the FEM) all the above mentioned effects should be taken into account (Fig. 2).
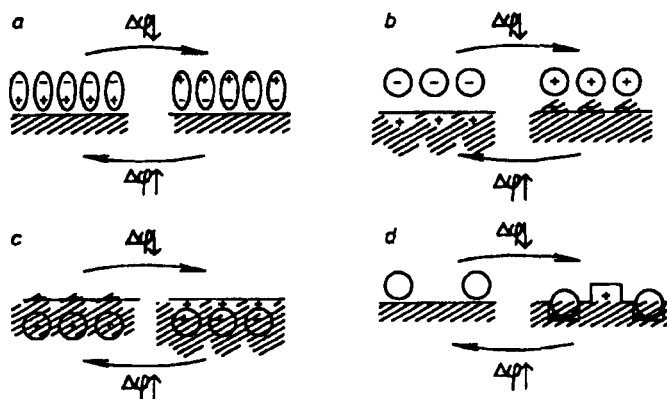

FIG. 1

Models for the interpretation of WFCs of metal surfaces due to the formation of various types of dipole layers: *a* adsorbed permanent or induced dipoles, *b* adsorbed charged particles, *c* incorporated charged particles, *d* reconstruction of the surface due to chemisorbed particles. The symbols $\Delta\varphi\uparrow$ and $\Delta\varphi\downarrow$ denote the increase and the decrease of the work function with respect to clean surface
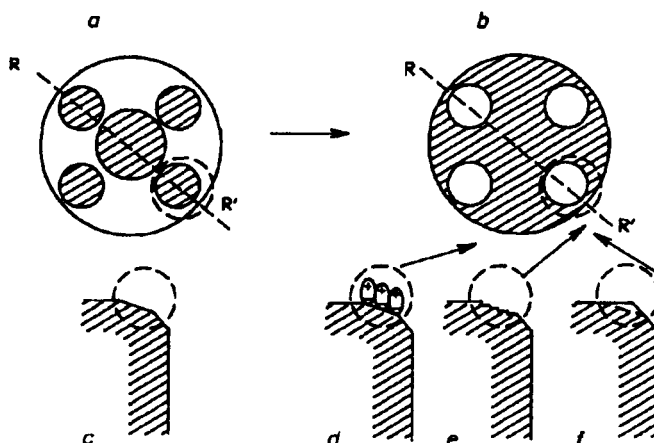

FIG. 2

Schematic view of FEM image of a sample surface (*a*) and of its change after a surface process (*b*). Part *c* shows silhouette of the sample along the line RR′ (see *a*); possible interpretations of the increased brightness (increased emission) in the circled region of the tip after the surface treatment (adsorption on a given plane (*d*), surface reconstruction of that plane (*e*), formation of an edge E (remoulding of the tip) which increases the field in its neighbourhood and thereby also the emission from it (*f*)

EXPERIMENTAL

The investigation was performed in a standard glass FEM which was attached to an all-glass ultrahigh vacuum system[2]. Clean surface of the tungsten tip was obtained by multiple heat treatment ($T = 2\,600$ K, $t = 1$ s, $p \leq 4 \cdot 10^{-8}$ Pa). The tip was annealed by the electric current passing through a loop to which the tip was spotwelded. The temperature was estimated from the heating current and voltage (measured at the center of the loop) on the basis of calibration by a pyrometer. The uncertainty of the temperature measurement was about 50 K. Oxygen from British Oxygen Co. Ltd. was introduced to the apparatus via a metallic leak valve.

RESULTS AND DISCUSSION

Tips thermally treated in the presence ($F = 2.7 \cdot 10^7$ V/cm, $T = 1\,800$ K) and in the absence ($F = 0$ V/cm, $T = 2\,400$ K) of a high electric field were used in these experiments. Presence of the field during the heat treatment caused the change of the hemispherical tip (obtained in the heat treatment without field) into a polyhedral tip (see e.g. ref.[5] and references therein; Fig. 3).

Figure 3 proves that the high-temperature high-field treatment (HT–HF treatment) does not influence the basic character of the image. The size of (100) and (211) planes is increased only in comparison with those planes on a tip treated at high temperature (HT) in absence of the electric field. It can be thus concluded that the extent of stepped and of atomically flat regions is different on the two types of samples.

Adsorption Experiments

Stepped ("open") surfaces exhibit usually higher reactivity than atomically flat surfaces. The first oxygen portions penetrate from the edges (stepped region) under the

a   b

Fig. 3

FEM images of a clean tungsten surface, prepared by heat treatment in absence (*a*) and in presence (*b*) of a high electric field: *a* heat treatment (HT) at $T = 2\,400$ K, *b* heat treatment at $T = 1\,800$ K and $F = 2.7 \cdot 10^7$ V/cm (HT–HF)

surface layer of a flat plane[6,7] lowering its WF. This effect might be responsible for the "disappearence" of the black spot corresponding to the projection of a small (100) plane on a hemispherical tungsten tip exposed to oxygen. In this case chemisorbed oxygen can reconstruct a small (100) plane more easily than a larger one on a poly-hedral tip (Fig. 4).

The increased reactivity of stepped areas surrounding a flat plane can be observed also in the case of (110) and (211) planes. The vicinal stepped region again facilitates reconstruction of the high WF (110) and (211) planes (Fig. 5) due to oxygen exposure of the tip. In this way the bright circle around (110) plane on a hemispherical tip can be understood (Fig. 5a), as well as the slightly enhanced emission from (211) plane and from broad terraces around the real (110) plane (Fig. 5c). On the other hand, only less pronounced effects of oxygen adsorption can be observed on polyhedral tips, which exhibit larger (110) and (211) planes, surrounded by smaller "open" (stepped) regions (Figs 5b, 5d).

Final FEM images of the tungsten tip exposed to about* 40 L of oxygen are both for hemispherical and polyhedral tip very similar to each other (Fig. 6) with the exception of (211) regions. In contrast to small (211) planes on a hemispherical tip, (211) planes
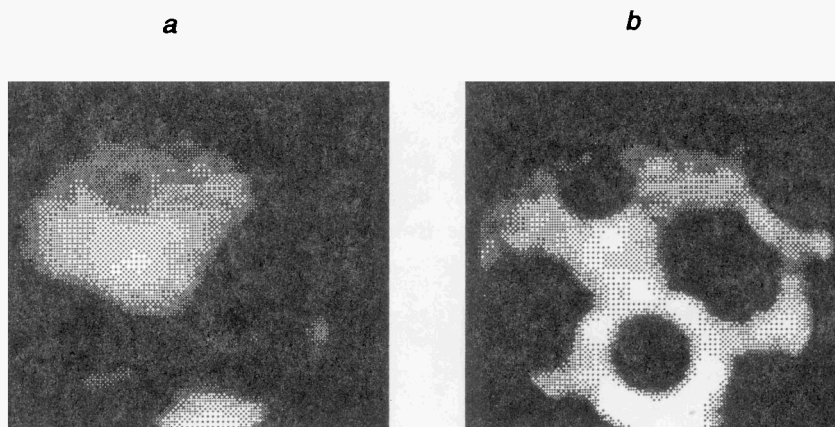
a   *b*

FIG. 4

FEM images of tungsten prepared by HT (*a*) and HT–HF (*b*) treatment, exposed afterwards to oxygen atmosphere at $T = 300$ K (*a*: 3 L*, *b*: 4 L*)

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* 1 L = 1 Langmuir = $1.33 \cdot 10^{-4}$ Pa s corresponds to the exposure of a sample for 1 s at a pressure of $1.33 \cdot 10^{-4}$ Pa.

on a polyhedral tip were the largest of all high WF planes (cf. Fig. 3). Consequently, they exhibited a higher stability. The above presented results suggest that the interpretation of the FEM image changes in the course of tungsten tip interaction with oxygen can be based on the microscopic reconstruction and/or adsorption effects rather than on the macroscopic remoulding of the tip apex under the given conditions. At higher temperatures the extension of densely populated high WF areas on account of atomically rough regions (facetting) was observed in the system (O_2 + W) already long ago[8] [− 12]. Our experiments indicate that the exposure exceeding 40 L of oxygen is sufficient for facetting the tungsten tip already at room temperature. The exceptional behaviour of
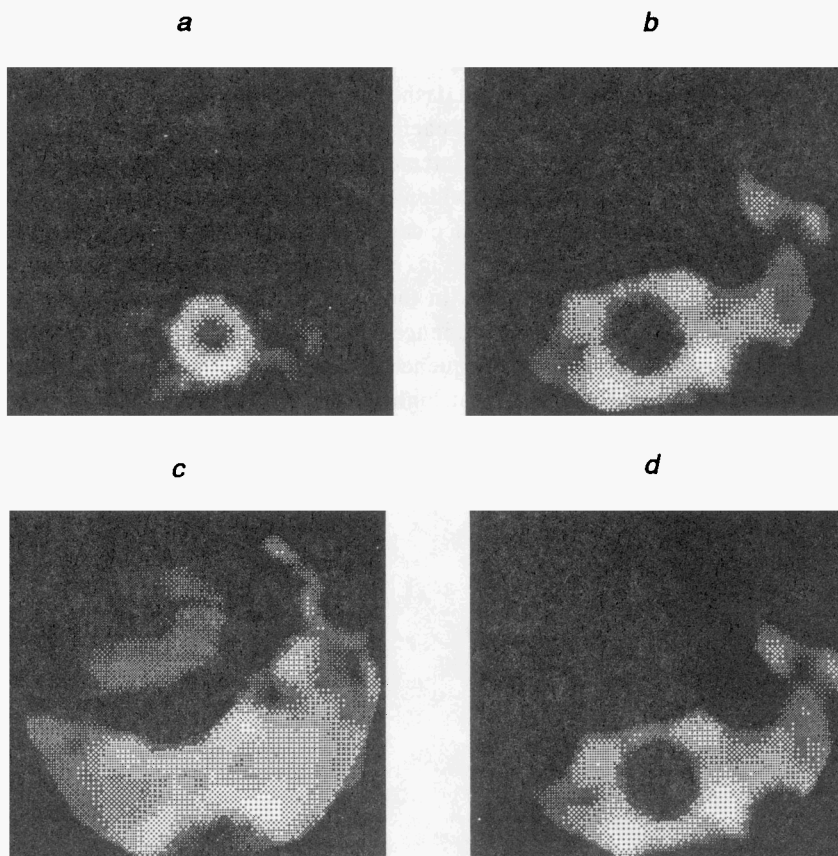

FIG. 5

The effect of the size of high WF (densely populated) planes of tungsten onto the extent of their interaction with oxygen. Hemispherical (**a**, **c**) and polyhedral (**b**, **d**) tips were exposed to approximately 20 L (**a**, **b**) and 30 L (**c**, **d**) of oxygen at T = 300 K

(211) regions in comparison with (100) and (110) areas may be related to a different character of the former regions (see Fig. 7) which are not atomically flat. The qualitative difference between low and high oxygen exposures of tungsten can also be exemplified by experiments of Bradshaw et al.[13]. At 2 200 K they observed only desorption of oxygen atoms from tungsten surface exposed at $T < 373$ K to 2 L of oxygen, whereas higher exposures resulted in desorption of tungsten oxides at temperatures even lower than $T = 2$ 200 K.

Desorption Experiments

Thermal desorption of oxygen from both hemispherical and polyhedral tips is compared in Fig. 8. Both tips were initialy exposed at room temperature to 27 L of oxygen. Desorption was performed by 1 + 2 s flashes to temperatures given in Fig. 8. The sequences of FEM images are similar to each other for both types of surfaces. This is not surprising, because oxygen strongly interacts with tungsten surface already at room temperature (surface reconstruction). Evidently, after heating to higher temperatures (1 600 – 1 700 K) no significant difference can be observed between oxidized tungsten surfaces, treated at HT and at HT–HF (Fig. 8). Obviously, thermal desorption is not simply a reversed process to adsorption in the O_2–W system. This can be seen when comparing Figs 4 – 6 and Fig. 8. The sequence of images of individual desorption steps does not correspond to the reversed sequence of images of the preceding adsorption steps. This is understandable, because at higher temperatures – provided that there is
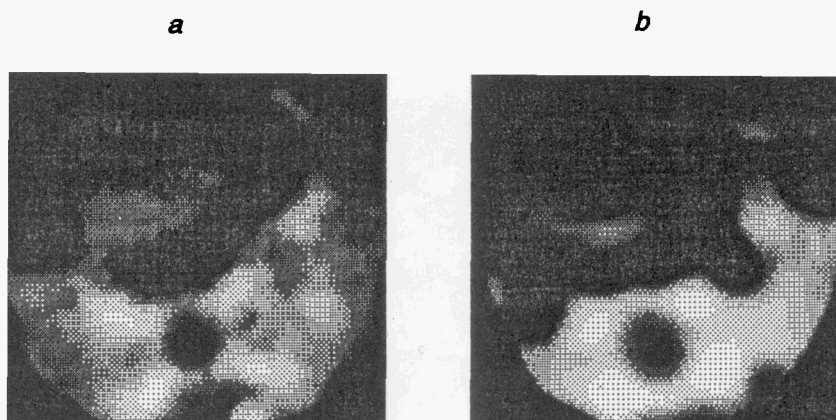
a   b

Fig. 6

Comparison of hemispherical and a polyhedral tungsten tips after their exposure to 45 L (*a*) and 38 L (*b*) of oxygen at $T = 300$ K

enough oxygen in the surface layer – some thermally activated processes can easily occur, as are oxide formation and oxygen incorporation into the tungsten lattice.

Desorption from (100) Plane

The emission changes in the (100) region are particulary interesting. After heating the tip to about 1 700 a bright circle appears around the (100) plane which afterwards shrinks so that the dark spot (image of the (100) plane) disappears. As soon as the bright circle around the (100) plane vanishes, a bright rhombus appears – corresponding to the real shape of the (100) plane (compare the model of the tungsten tip in ref.[14]).
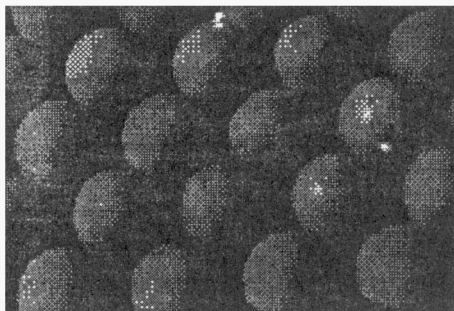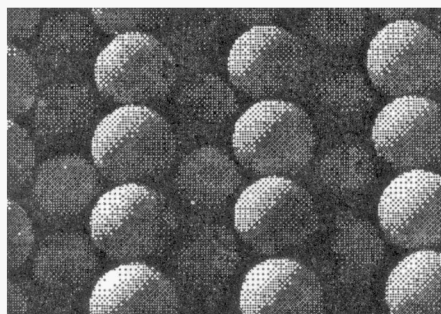

a
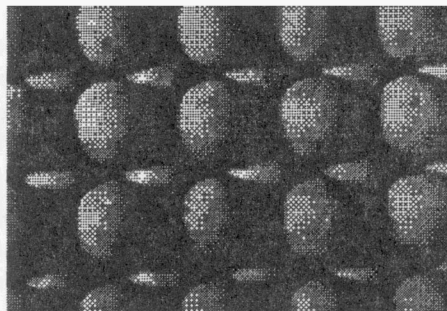
b

c

Fig. 7
Models of *a* (100), *b* (110) and *c* (211) planes on the tungsten surface

A similar effect, viz. the appearance of bright rhombus in the place of (100) plane has been observed in the (N_2–W) system[15]. An analogical "developing" of the image of the real (100) plane occurs due to lowering the WF in the vicinal stepped region resulting from physisorption of argon[16]. The (100) plane appears in this case as a dark rhombus. The above described behavior of the (100) region on oxidized tungsten tip has been observed in other FEM studies[9,17,18], too. However, no detailed interpretation has been presented. We observed the bright rhombus after flashing the (W + O_{ads}) system to about 1 900 K (Fig. 8). At still higher temperatures further bright regions appear and finally a clean tungsten surface is obtained (Fig. 3a), identical for both types of surfaces.

For understanding the emission properties of (100) region, it is useful to summarize some results in literature. King, Madey and Yates[19] studied oxygen interaction with polycrystalline tungsten. They found the following steps in the desorption from a layer of oxygen formed by exposure to 40 L at room temperature: (i) desorption of tungsten oxides (1 400 – 1 900 K), (ii) desorption of oxygen after completion of WO_x desorption (2 100 K). From these they suggested a model of heavily oxidized tungsten surface (Fig. 9). Because of the polycrystallinity of the sample the mentioned authors were not able to discern atomic details of the mechanism of the tungsten–oxygen interaction.

The study of Wells and King[20] is directly related to our problem of the (100) region. The authors studied a macroscopic (100) plane of tungsten in the interaction with a molecular beam of oxygen in the temperature range 300 – 2 200 K. At $T > 1$ 700 K and a coverage higher than about 0.7 of oxygen monolayer a circular trace of the beam appeared as a low WF area (WF lower than that of the clean (100) plane). The authors explained this effect by desorption of tungsten oxides (WO_x) at those temperatures, leaving the surface layer with incorporated chemisorbed oxygen. At the initial oxygen coverages lower than half of a monolayer, low WF area could be observed already at T > 1 400 K.

The atomic structure of (100) plane of tungsten covered by about half of oxygen monolayer and heated to higher temperatures was found to be (2 × 1) by LEED[21 – 25] and by ion scattering[26]. Some authors suggested[3,21 – 23] that lowering of the WF value observed under the given conditions, was due to roughening of the (100) plane induced by oxygen chemisorption rather than by oxygen incorporation into the tungsten lattice. Such an explanation, however, accounts neither for desorption of tungsten oxides at temperatures lower than those needed for desorption of oxygen atoms, nor for the increase of the yield of O^+ in electron stimulated desorption after repeating oxygen adsorption onto the (2 × 1) reconstructed oxidized (100) plane of tungsten[25]. Some authors[21,23,24] explained the lower value of the WF of (2 × 1) structure of the oxidized (100) plane (compared) with clean (100) plane) by assuming the ionic radius of O^- to be smaller than that of tungsten. This assumption, however, is not correct[27]. The argumentation[23] is based on oversimplified model calculations (oxygen atom placed at the
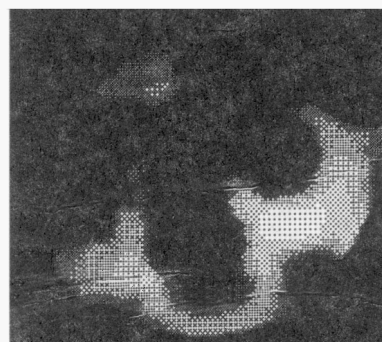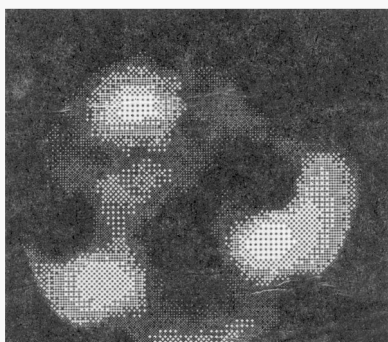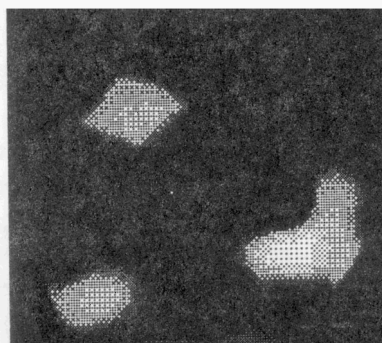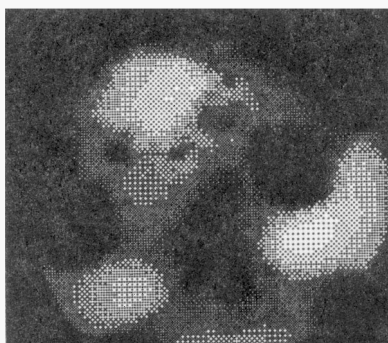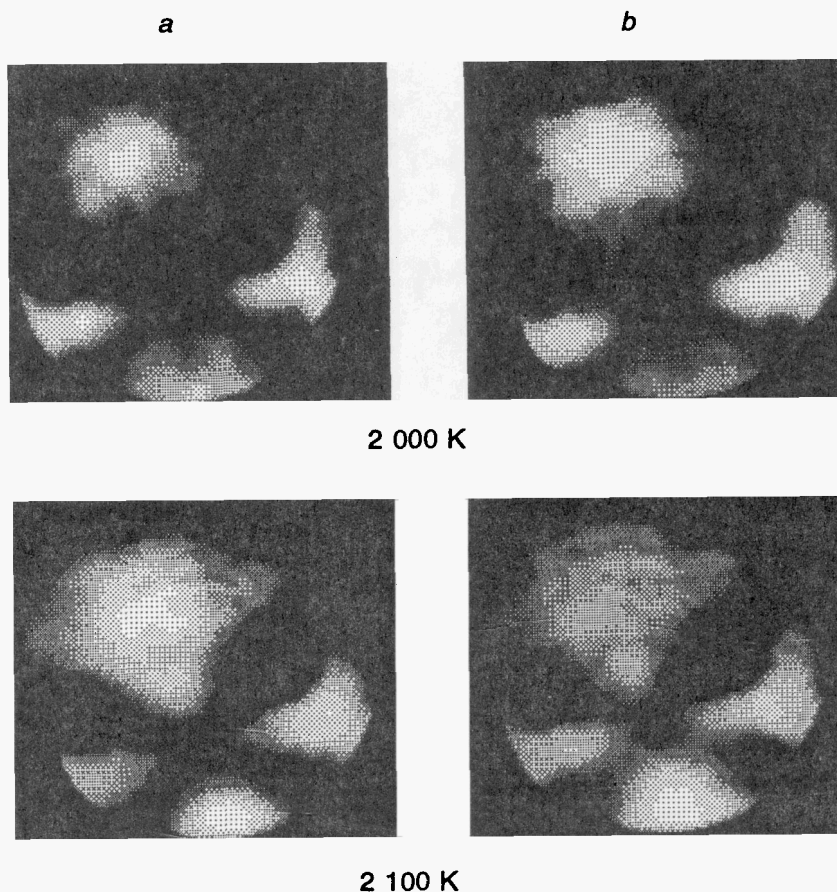
a
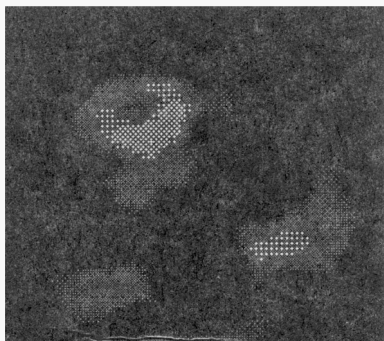
b
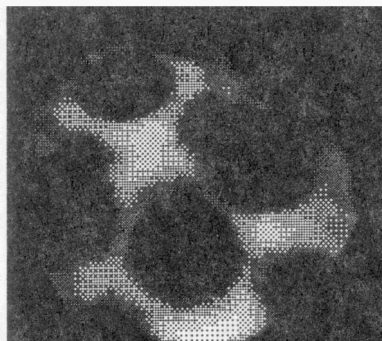
1 700 K

1 800 K

1 900 K

FIG. 8
Thermal desorption of oxygen from hemispherical (*a*) and polyhedral (*b*) tips at 1 700 to 2 100 K

center of a bipyramide formed by 6 tungsten atoms) used for the interpretation of EELS data. Moreover, the LEED and MBS experiments of Hinch et al.[6] seem to strongly support the incorporation of oxygen: after heating the (100) plane of tungsten covered by oxygen to more than half a monolayer the LEED indicated the (2×1) structure, whereas molecular beam scattering of helium (sensitive to the atomic structure of the surface plane only) evidenced the (1×1) structure of clean (100) tungsten plane.

Based on the above described FEM results and taking into account the literature data one can propose the following model of the surface reconstruction of the (100) tungsten

plane by oxygen adsorption at higher temperatures (Fig. 10). The amount of oxygen incorporated into the surface layer can be roughly judged from the decrease of the WF which was observed only when the oxygen coverage was about half a monolayer[20] (in agreement with data in refs[21 – 24]). Reconstruction of small planes, surrounded by stepped regions, is easier compared with the large ones.

The effect of steps which have the role of "entrance gates" for incorporation, was suggested already earlier[6,7]. In our opinion half a monolayer of oxygen is burried under
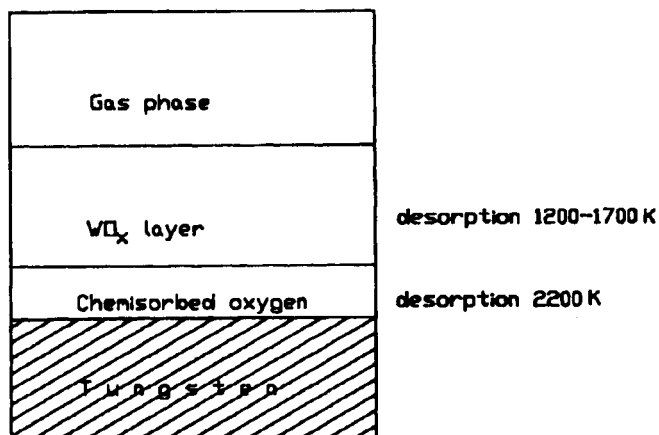

Fig. 9
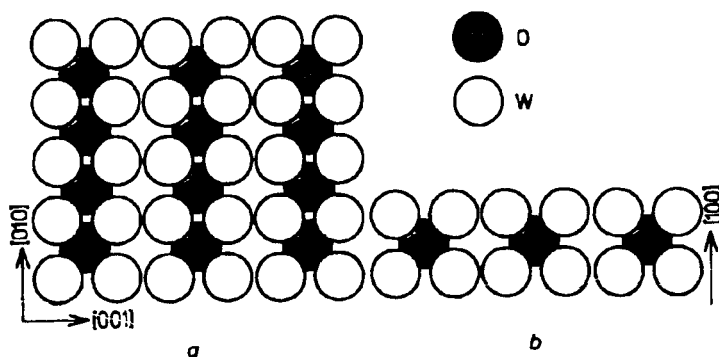Simplified model of a heavily oxidized tungsten surface (after King, Modey and Yates[20])

Fig. 10
Model proposed for reconstruction of the (100) tungsten plane due to incorporation of half of oxygen monolayer after heating to higher temperatures: *a* top view, *b* side view

the first layer of tungsten and forms there (2×1) structure (Fig. 10). The excess oxygen (exceeding one half of a monolayer) forms an oxidic bond with the tungsten atoms in the outermost layer, which are then less strongly bound to the rest of the solid. Consequently, WO_x desorbs at lower temperatures than oxygen itself. At the temperature of WO_x desorption the incorporated oxygen moves and this again leads to low WF surfaces (Fig. 1c). This is the reason why WFC reverses its sign just after WO_x desorption is completed (compare Figs 8a and 8c). If the temperature exceeds 2 000 K desorption of the incorporated oxygen can be observed[19].

CONCLUSIONS

FEM study of the oxidation of two types of tungsten tips (hemispherical and polyhedral tips) has elucidated some problems of oxygen interaction with stepped and atomically flat surfaces. In agreement with literature it has been confirmed that edges and stepped regions represent an "entrance gate" for the incorporation of oxygen into the tungsten lattice under the densely populated surface layer of the metal. The hemispherical tips represent surfaces with high concentration of atomic steps surrounding small densely populated planes. Consequently, interaction of these surfaces with oxygen is more intensive than that of of macroscopic planes. On the other hand, polyhedral tips expose to the gas phase atomically flat planes separated only by restricted stepped regions. As a result, these surfaces exhibit higher stability with respect to the oxygen attack. These effects were particulary clear-cut in the (100) region. A model for the reconstruction of this particular plane on the FEM tip surface has been formulated.

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