Field Emission Microscopic Observation of Effects of Oxygen or Air on the High Temperature Tungsten Cathode

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Synopsis

By using Müller-type field emission microscope with an ordinary pumping system, effects of gas introduction and filed desorption on a carbon-adsorbed tungsten surface are examined at high temperatures around 1500°K. The removal of carbon from the tungsten surface is verified when a very small quantity of oxygen or air is introduced into the tube. The carbon-adsorption on the tungsten surface caused by the decomposition of vacuum oil on the tip under the conventional operating condition is observed successively during the process. From the results, it is found that the change in the 011 and the 111 regions is always regular, but in the 001 region it is very complicated. The field desorption effect on the carbon-adsorbed tungsten surface is also observed, and the same change as obtained in the gas introduction is found in the 001 region.

I Introduction

When the point cathode is used as the electron source of an electron microscope or of an electron diffraction camera, it is very important to know the character of the electron emission from the point cathode.(1) Almost all the field emission microscopic observations of tungsten have hitherto been performed in ultra high vacuum(2). Since the electron microscope or the electron diffraction camera is operated in the ordinary vacuum system with an oil diffusion pump, it is necessary to observe the filed emission pattern of the tungsten point cathode in the same vacuum condition. From this point of view, we(3) previously observed the dependence of the emission pattern of tungsten on temperature in ordinary vacuum by using the filed emission microscope with glass joints. It was consequently found that the two different kinds of pattern existed; namely, the "high temperature pattern" observed after heat treatment above 2300°K shown in Fig. 1 (a) and the "low temperature pattern" observed after heat treatment under 2300°K shown in Fig. 1 (b). The low temperature pattern was supposed from its six-fold symmetry to be the pattern of the tungsten carbide, while the high temperature pattern was considered to be the pattern of the carbon adsorbed tungsten produced

* A graduate student of Faculty of Science. This work was done under the instruction of Professor T. Hibi.

(1) For example, T. Hibi: J. Electronmicroscopy, **4** (1956) 10.

(2) For example, R.H. Good jr. and E.W. Müller: Handbuch der Physik, **21** (1956) 176.

(3) F. Okuyama and T. Hibi: Japan. J. appl. Phys., **4** (1965) 337.

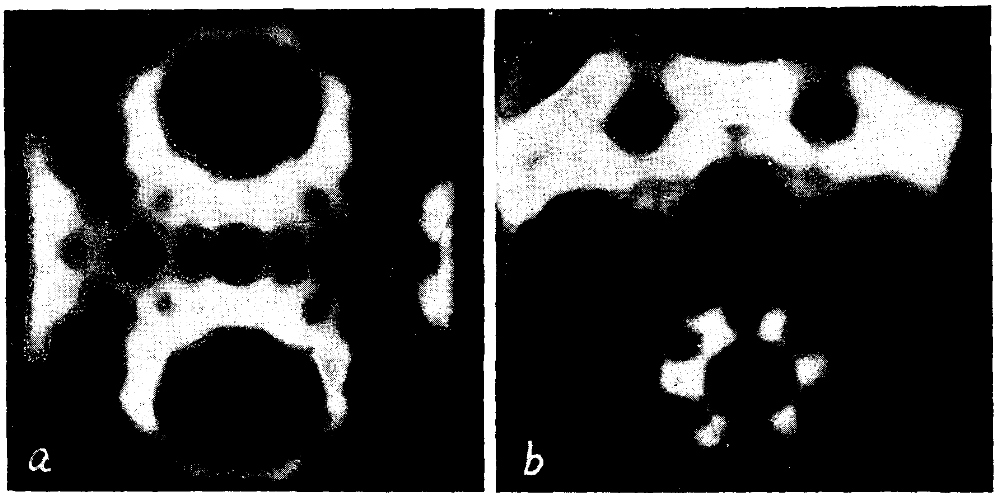

Fig. 1. High temperature pattern (a) and low temperature pattern (b).

by decomposition of vacuum oil on the tip. If this consideration is correct, it will be expected that the clean-up of the tungsten surface will temporally occur by introducing a very small quantity of oxygen or air into the tube when the surface is in the state corresponding to the high temperature pattern. To verify this, a small quantity of oxygen or air was introduced. The clean-up of the tip surface and some other interesting phenomena were consequently observed.

The field desorption effect on the carbon-adsorbed tungsten tip was also examined, and the same change as that seen in the gas introduction was observed in the 001 region.

These experimental results are reported in this paper.

2 Experimental Method

A tip of the point cathode having a radius of curvature of 0.1–1μ was made by electrolytic etching from tungsten wire 0.126 mm in diameter under the condition of NaOH 1 normal and 70–80 V.D.C. A Müller-type electron emission micro-

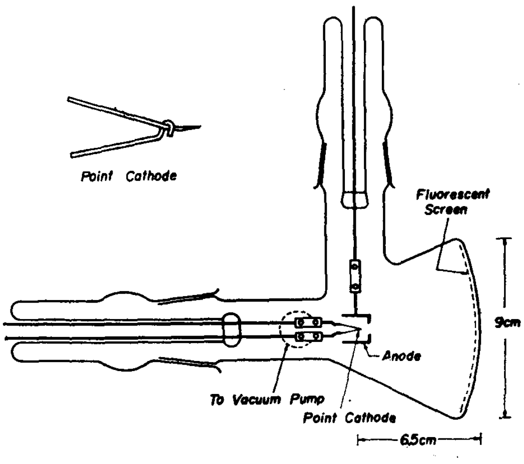

Fig. 2. Experimental tube.

scope almost same as that used in the previous experiments[(3),(4)] was used (Figure 2). The cathode was placed in a cylindrical anode 13 mm in length and 13 mm in diameter with a center hole 6mm in diameter in the basic plate. The anode voltage was 3–5 KV, the diameter of the fluorescnet screen 90 mm and the distance between the tip and the fluorescent screen 65 mm. The glass joints were used for changing the cathode and cleaning the anode. Vacuum of about 10^{-5} Torr was obtained by an ordinary oil diffusion pump and a rotary pump. Oxygen or air was reserved in a gas vessel, and it was introduced through a cock into the field emission microscope tube by small quantities, if necessary.

3 Experimental Results

Fig. 3 (a) shows the filed emission pattern of a ⟨011⟩-oriented tungsten tip adsorbed by carbon. In general, the tip of the body-centered cubic crystal has the similar ⟨011⟩-orientation as this case. Figure 4 represents the orthographic projection of the ⟨011⟩-oriented tip. When the tungsten tip had the surface state shown in Fig. 3 (a), a small quantity of oxygen was introduced into the field emission microscope tube. The pattern of a comparatively clean surface was consequently obtained as shown in Fig. 3 (b).

In addition to the observation of the abrupt change from the carbon-adsorbed surface to a comparatively clean one, shown in Fig. 3, the slow change in the surface caused by the carbon-adsorption was also examined. Figure 5 shows the result. In this case the tungsten tip had the ⟨001⟩-orientation accidentally, though the ordinary tungsten tip has the ⟨011⟩-orientation. Figure 6 represents the orthographic projection of the ⟨001⟩-oriented tip. Fig. 5 (a) is the emission pattern of the ⟨001⟩-oriented tungsten tip adsorbed by carbon. The pattern of the perfect carbon-adsorbed tip has quite dark areas around the {001} planes as shown in Fig. 3 (a). On the contrary, in this pattern the 001 region reveals the

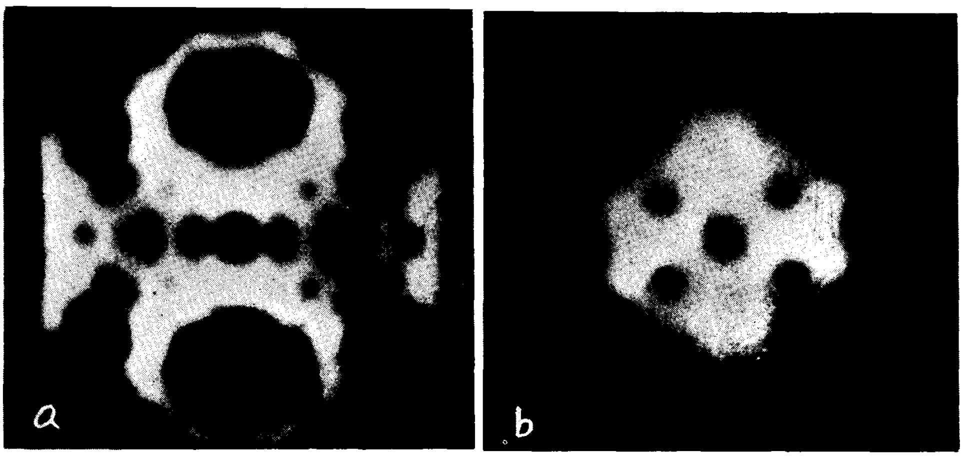

Fig. 3. Clean-up of the carbon-adsorbed tungsten surface. (a) and (b) are the emission patterns obtained before and after the introduction of oxygen, respectively.

(4) T. Hibi and K. Ishikawa: Sci. Rep. RITU, **A13** (1961) 299.

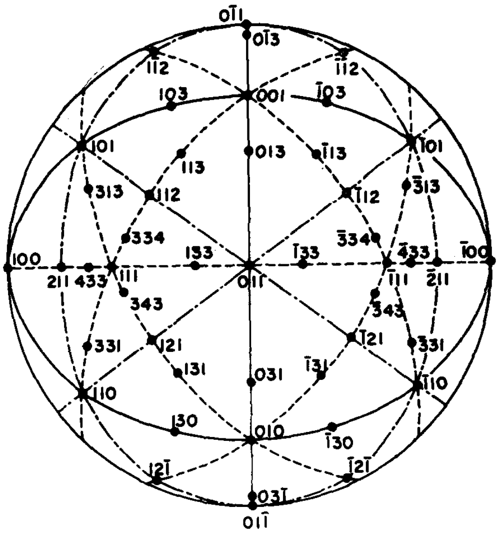

Fig. 4. Orthographic projection of the ⟨011⟩-oriented tip.

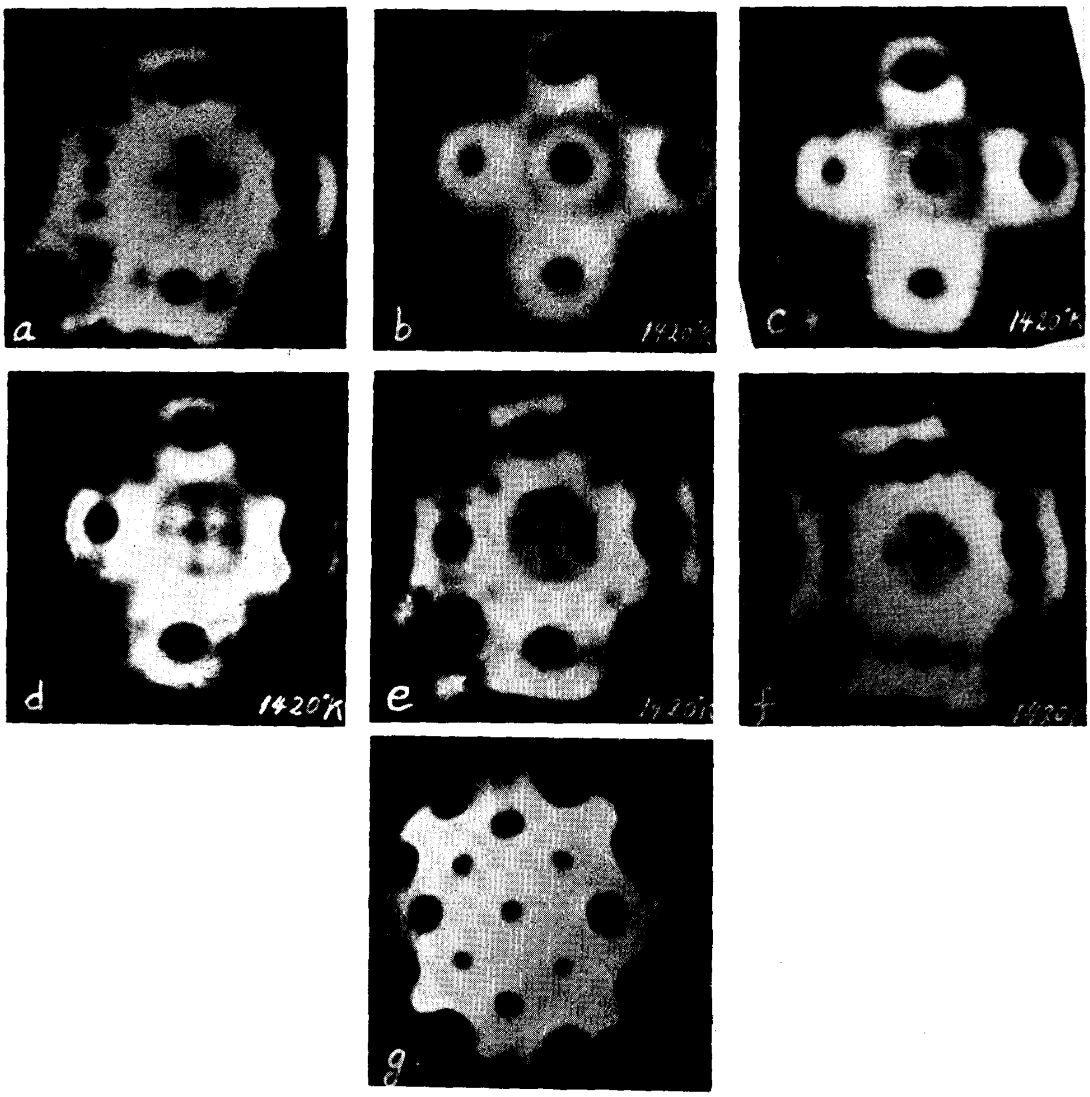

Fig. 5. An example of oxygen effect on the ⟨001⟩-oriented tip.

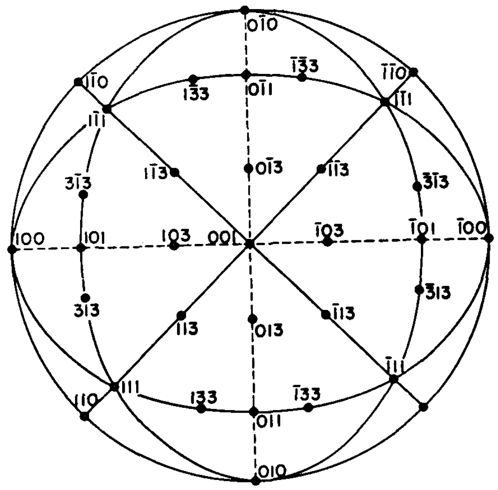

Fig. 6. Orthographic projection of the ⟨001⟩-oriented tip.

details. Therefore, it seems that the quantity of carbon adsorbed on the tip surface is comparatively small in this case. After introducing a very small quantity of oxygen at room temperature, the pattern in Fig. 5 (b) was obtained at 1420°K. The characteristics of this pattern are that the 111 region and the (001) plane are dark, that a dark ring can be seen on the 001 region, and that the {133} planes which are dark in (a) are bright. In the both cases of the clean and the comparatively clean surface, the 111 region is bright. It is supposed, therefore, that the removal of carbon from the tip surface was not sufficient in this case.

When the tip was kept at 1420°K, the successive changes from (c) to (e) were observed. In pattern (c), the cross lines connecting the {013} planes ([001] zone lines) faintly appeared, the {133} planes began to appear and the {113} planes were observed as the dark faces. In Pattern (d), the [001] zone lines became clearer, the darkness of the {133} planes increased and the {013} planes became distinguishable. With the progression of the carbon-adsorption, the {113} planes became bright and the electron emission at the four corners of the 001 region increased, as shown in Pattern (e). At the same time, the emission at the 001 region decreased. Pattern (f) was obtained after the further progression of the carbon-adsorption. This pattern is quite similar to Pattern (a) except for the 001 region. The completely clean tip surface could be obtained by introducing a proper quantity of oxygen in this state, as shown in Pattern (g). From this experiment, it becomes evident that a dark ring appears around the (001) plane by introducing a very small quantity of oxygen into the tube.

Figure 7 shows another example of the change caused by the introduction of a small quantity of oxygen into the tube. Pattern (a) represents the emission pattern of the perfectly carbon-adsorbed tungsten tip having the same ⟨011⟩-orientation as that of Fig. 1 (a). After the introduction of a small quantity of oxygen at room temperature, Pattern (b) was obtained at 1420°K. It is the characteristic of this pattern that the 111 region and the {133} planes are bright.

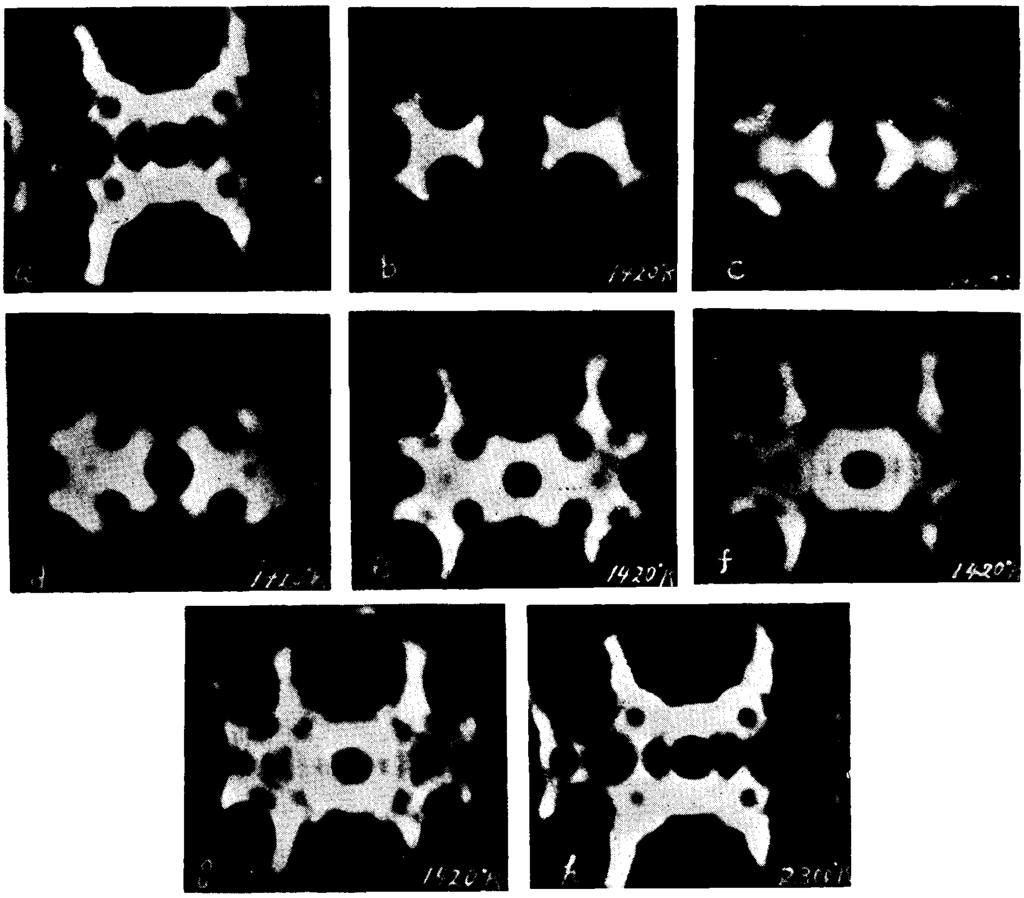

Fig. 7. A typical example of oxygen effect.

This fact suggests the complete removal of carbon from the 111 region and the {133} planes. The results of the successive changes due to the heat treatment at 1420°K are shown in Patterns (c)-(g). The characteristics of these changes are as follows; in the 111 region and the {133} planes, the carbon-adsorption immediately occurs, while in other regions it leisurely follows, by way of the process of the slow cleaning. That is, in Pattern (c), the lines connecting the {112} planes ({112}-bands) became dark because of the carbon-adsorption. In Pattern (d), the {111} planes also became dark owing to the carbon-adsorption, while the upper and lower portions of the (011) plane became slightly bright because of the cleaning of these parts. In Pattern (e), the {133} planes became dark and the emission at the regions around the {011} planes was greatly increased by the cleaning of these areas. With the progress of the carbon-adsorption, the emission from the whole 111 region decreased and the two {133} planes at the both sides of the (011) plane become dark as seen in Pattern (f). These facts suggest the occurrence of the carbon-adsorption in the 011 region. With further progress of the carbon-adsorption, Pattern (g) similar to Pattern (a) was obtained. In Pattern (g), the {334} planes appeared as the dark faces. This fact suggests the carbon-adsorption on tungsten. After a high temperature heat treatment for a short time, Pattern (h) which is quite similar to Pattern (a) appeared.

In the case of the introduction of air into the tube, a little different change from that in the case of the introduction of oxygen was observed. Figure 8 shows the change, which appeared when a small quantity of the introduced air remained as the residual gas (of about 10^{-4} Torr) in the tube because of insufficient out-gassing of the tube. When a large amount of air was introduced into the tube, Pattern (a) of the perfect carbon-adsorbed tip changed to Pattern (b), which was quite similar to the pattern of the oxygen-contaminated tungsten tip. After a high temperature flash, Pattern (c) same as the pattern in Fig. 7 (b) was obtained. When the residual air was present in the tube, the pattern changed from Pattern (c) to Pattern (e) by way of Pattern (d), which has the bright {001} planes. The same pattern as Pattern (c) appeared after high temperature flash in the state of (e). However, it came back to the gas-contaminated pattern, Pattern (e), by way of same process if the tip was kept in residual gas. By repeating flashing, quite the same process as that of (b)-(e) could be observed. That is to say, this process was reproducible when residual gas was present in the tube.

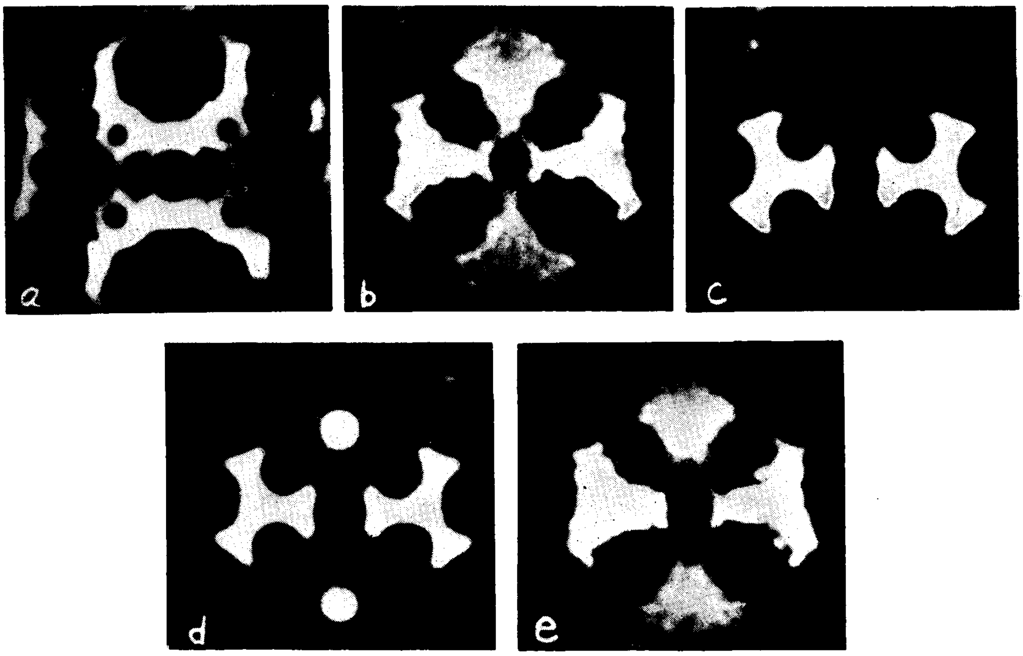

Fig. 8. Change of the emission pattern in the presence of a very small quantity of air.

When the quantity of residual gas decreased and the effect of the gas became weak, the {001}-brightened pattern as in Fig. 8 (d) changed as shown in Figure 9. Pattern (a) is the same as the pattern in Fig. 8 (d) having the bright {001} planes. When the cathode was kept at 1470°K, the change from (b) to (e) occurred. In this case, the change in the 111 and the 011 regions was quite similar to that in the introduction of oxygen, while the change in the 001 region was very peculiar. That is, in Pattern (b), the bright areas around the {001} planes were enlarged, and at the same time the {001} planes became slightly dark temporarily. In Pattern

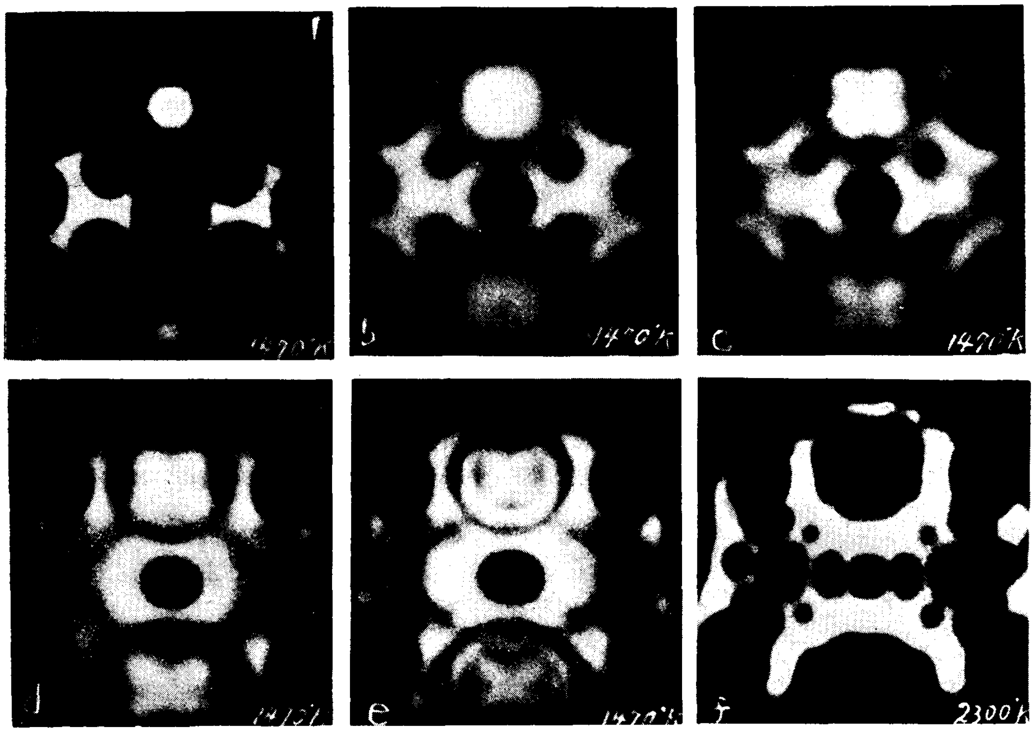

Fig. 9. Successive changes of the emission pattern having the bright 001 region.

(c), the dark [001] zone lines appeared. As the carbon-adsorption proceeded, the [011] zone lines in the 001 region became bright and the dark rings whose centers were in the {001} planes appeared as shown in Pattern (d) and Pattern (e). Pattern (e) is closely similar to the pattern of the perfect carbon-adsorbed tungsten tip. After the high temperature heat treatment for a short time, the pattern of the perfect carbon-adsorbed tungsten tip was obtained and the [001] zone lines disappeared, as seen in Pattern (f). From a comparison between Pattern (e) and Pattern (f), it is found that the [011] zone lines and the rings in the 001 region are seen only in Pattern (e). The appearance of these zone lines and rings may perhaps be due to the gas adsorption in the 001 region. That is to say, it may be considered that the effect of the residual gas cannot be completely eliminated in the case of Pattern (e).

If the above consideration is correct, it is expected that, by performing the field desorption of carbon from the tungsten surface in the presence of a small quantity of residual gas, the effect similar to the case in Fig. 9 (e) can be observed. Figure 10 shows an example of the field desorption effects. By performing the field desorption at 7.8 kilovolts for 10 minutes on the carbon-adsorbed tungsten tip, the pattern changed from (a) to (b). The appearance similar to the case of Fig. 9 (e) is clearly seen in the 001 region, as shown in Pattern (b). This change in the 001 region may be due to the adsorption on these areas of the released gas which was produced by the collision to the glass wall of the carbon ions desorbed from the tip surface.

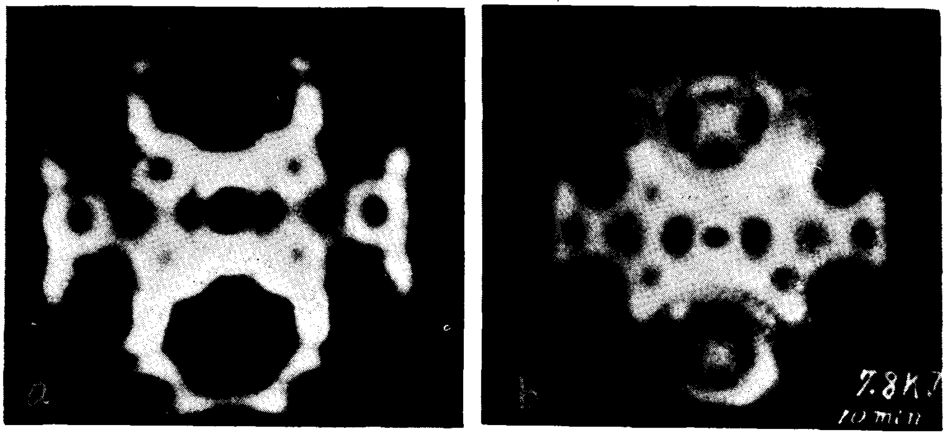

Fig. 10. Effect of field desorption in the presence of a small quantity of air.

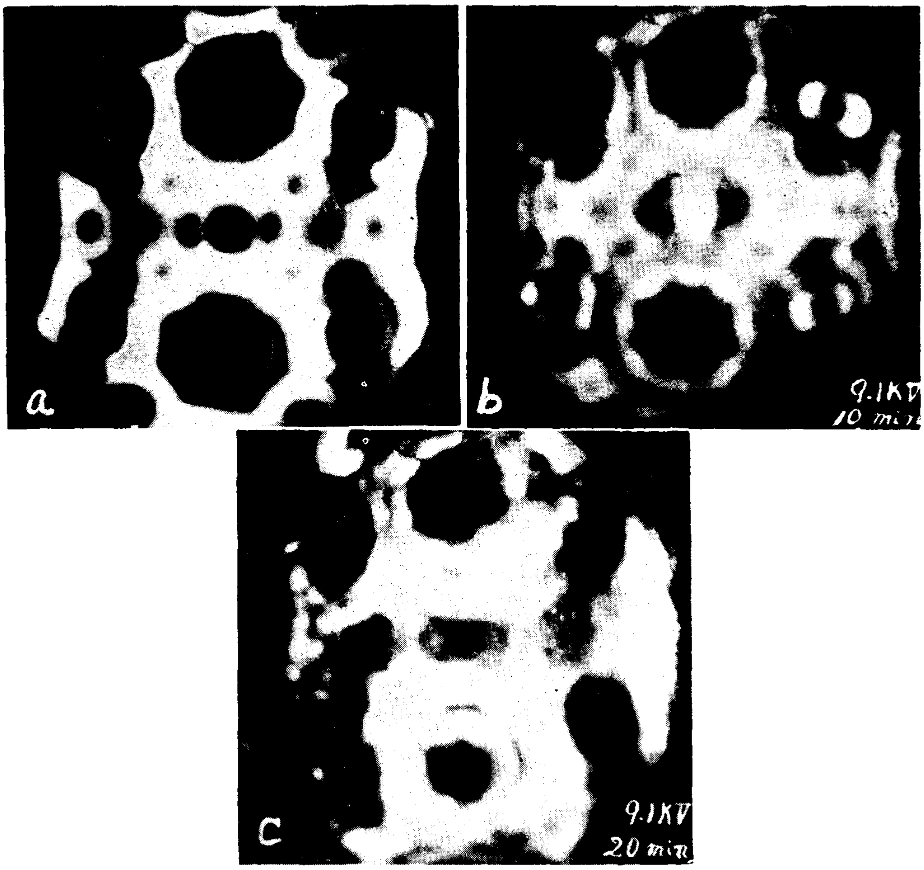

Fig. 11. A typical effect of field desorption.

When the residual gas was not present in the tube because of sufficient outgassing of the tube, the result in Fig. 11 was obtained in vacuum of about 10^{-5} Torr. By performing the field desorption at 9.1 kilovolts for 10 minutes on the complete carbon-adsorbed tip shown by Pattern (a), Pattern (b) was obtained. In this pattern, the rings are seen in the 001 region, but the [011] zone lines are not seen. It is also found that the emission from the areas around the {011} planes increases. With further field desorption for 10 minutes, the emission distribution became gradually uniform as shown in Pattern (c). This result suggests that the surface approaches the clean one. Such a change is considered to be the normal case of the field desorption effect.

4 Conclusion

From these experimental results obtained by introducing a very small quantity of oxygen or air into the tube, it is found that a clean-up occurs in the carbon-adsorbed surface of the tungsten tip. The carbon-adsorption process becomes clear with the emission patterns obtained successively during the process, and it is found that the change in the 011 and the 111 regions is always regular, but the 001 region shows the very complicated change. As a result of the field desorption on the carbon-adsorbed tungsten surface, it is verified that the change similar to that obtained in the gas introduction is seen in the 001 region.

The main subjects in many filed emission microscopic studies have been limited to making clear the properties of various crystal planes. By judging from the results of this study, however, it seems that the consideration of the zone lines is also very important to explain the various emission patterns obtained in this experiment. Such discussion and consideration will be published in detail on another occasion.

Acknowledgement

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