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FIM OBSERVATION ON THE REACTION OF METALS (W, Mo) WITH n-OCTANOL UNDER AN APPLIED VOLTAGE

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Résumé. Il a été montré que l'alcool n-octylque réagissait électrochimiquement non seulement avec le W mais encore avec le Mo en divisant la face (110) en quatre parties entre les lignes de zone [001] et [110]. Une étude détaillée des images consécutives d'évaporation de champs a montré qu'il y avait une fosse profonde faite à la face (110), la face la plus stable chimiquement des métaux b.c.c.

Abstract. An electrochemical reaction in n-octanol which splits the central (110) plane into four parts across the [001] and [110] zone lines has been shown to occur not only to W but also to Mo. A detailed study of the sequential images of field evaporation have revealed that there is a deep pit made on the (110) plane, chemically the most stable plane of b.c.c. metals.

1. Introduction.

In order to extend the capability of atomic resolution of field ion microscopy to the study of the initial stage of surface reaction of metals with various liquids, we have been investigating the reaction of tungsten with n-octanol [1, 2, 3, 4] and have shown that when a clean tungsten tip was immersed in n-octanol and a positive d.c. voltage of several volts was applied, it reacted with the alcohol to give various kinds and degrees of corroded surfaces depending on the condition of the application of the voltage (4). Specifically, when the tip immersed in the alcohol was subjected to a pulse with an amplitude higher than +5V, a rising time shorter than about 100nsec and a width of the order of one second, it was severely damaged to give a characteristic field ion images in which the central (110) plane was split into two across the [001] zone line or even into four across the [110] and the [001] zone lines (4).

In the present study, we have examined the detailed shape of a tungsten tip showing the split by means of sequential field evaporation. Preliminary results of the reaction of molybdenum with n-octanol under an applied voltage are also presented for comparison with tungsten.


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Fig. 1. A series of sequential images of W before and after the electrochemical reaction with n-Octanol. 
(a) Before; (b) (d) after.
2. Experimental.

A tungsten tip was cleaned by field evaporation, and it was immersed in n-octanol in a tiny glass cup inserted into the field ion microscope chamber through a side arm opening under a stream of Ar so as to keep the contamination of the tip surface with air to a minimum. After a certain voltage was applied to the tip, the glass cup was removed and the resultant tip surface was observed with the field ion microscope. A more detailed description of the apparatus and the procedure has been given elsewhere [41]. In order to observe the field evaporation sequence of the split central (110) plane in more detail, the tip was transferred to another field ion microscope equipped with a channel plate.

3. Results and discussion.

Figure 1 shows the sequential images of field evaporated surfaces of a tungsten tip after it was subjected to a pulse with an amplitude, +5V, a rising time, 10nsec, and a width, 3.2sec, while it was immersed in n-octanol.

As can be seen in Fig. 1 (b), the central (110) plane is severely damaged and is split into 4 or 5 parts. As the tip was field evaporated, they successively disappeared leaving normal step rings as shown in Fig. 1 (f). The number of the (110) planes field evaporated from (b) to (f) was about 35.

Figure 2 shows successive micrographs before and after Fig. 1 (d). It can be seen that the 6th single step ring counted from the central ring of the left (110) plane, which encloses both the two central (110) planes, indicated by an arrow in (a) is severely distorted inward in (b) after 3 and 4 layers of the left and the right (110) planes are field evaporated, respectively, and is finally separated into two parts in (c) and (d). Field evaporation of 13, much more than 6, layers of (110) plane from (a) was necessary to reach the normal single (110) plane. Such an evaporation behavior suggests that the topography of the tip end in (a) is somewhat like one shown by a schematic drawing given at the bottom of Fig. 2. The outermost circle corresponds to the 6th step ring shown by the arrow in Fig. 2 (a). Between the two (110) hills, there is a deep pit with a depth of 7 atomic layers beneath the hatched plane. Both the outer hatched step and the doughnut-like hatched one in the central pit belong to the same (110) layer. This model well explains the field evaporation behavior as shown in Fig. 2.

The split images were obtained only when the width of a pulse or the total length of the width of successively applied pulses reached the order of 1 sec (I). The split images were not obtained merely with the application of pulses with a short rising time or merely with the application of a certain voltage for more than around 1 sec. The application of 100 pulses with a rising time, 10nsec, and a width, 150nsec, did not give rise to the split images. These facts suggest that the change observed in the present study needs both a short rising time of pulses as a trigger and a long time of the applications of certain voltage for the progress of the reaction. This means that
the reaction is not a fracture of a part of a tip but a kind of electrochemical reaction of metal with n-octanol.

It is quite interesting and puzzling that the \{110\} plane most drastically damaged in this study is well known to be one of chemically the most stable planes of b.c.c. metals.

In order to see whether or not this reaction is specific only to tungsten, a molybdenum tip was treated similarly as tungsten. Figure 3 shows the sequential images of a molybdenum tip after it was subjected to a similar pulse with +12V as those applied to tungsten during it was immersed in n-octanol. The central \{110\} plane is split across the [001] zone line into two parts and there are in addition T-shaped valleys on the \{310\} and \{130\} planes whose each branch is directed toward the centers of the peripheral \{110\} planes. As field evaporation proceeded, the valleys became shallower. In another case where the pulse voltage was +15V, the central \{110\} plane was split into 4 parts across the [110] and [001] zone lines as shown in Fig. 4. With further evaporation, two of them disappeared, leaving two parts across [110] zone line. Unfortunately, however, the tip had jumped during field evaporation before the normal surface was recovered in either case above. These results, however, suggest that the electrochemical reaction giving rise to the split of \{110\} plane is a reaction characteristic of both W and Mo.

As has been described, W and Mo seem to react with n-octanol under a certain applied voltage with a pulse as a trigger for the reaction. The most severe change in the image is obtained on the most stable crystal plane. A further investigation on earlier stages of the reaction is necessary to elucidate the initial mechanism of the reaction. The study along this line is now in progress.

References

Fig. 2. A series of sequential images of W before and after (d) in Fig. 1, and a schematic drawing of the topography of the tip end in (a). (b) is the same image as (d) in Fig. 1.
Fig. 3. A series of sequential images of Mo before and after the electrochemical reaction with n-octanol.
(a) Before; (b) (d) after.

Fig. 4. Another series of sequential images of Mo before and after the electrochemical reaction with n-octanol.
(a) Before; (c) (e) after.