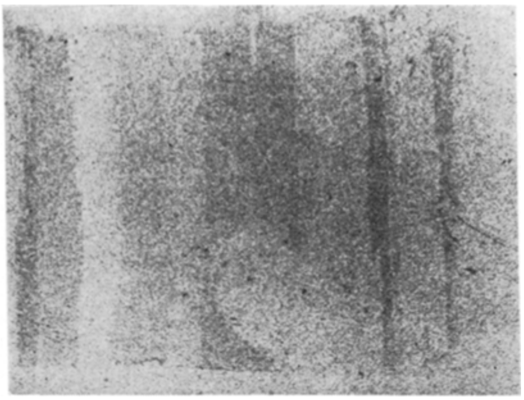

Fig. 4. A Berg-Barrett image of an electrodeposit formed at 99°C on the substrate shown in Fig. 2. X15. The images in Fig. 2 and 3 are formed by the same Laue diffraction spot; the image in Fig. 4 is formed by a different Laue spot.

graphic plates were placed within 1-3 mm of the specimen to record the image. Angles of incidence of 10°-15° were used, and these gave substrate contributions to the image of less than 2%. Exposure times of 30 min were used.

Cliffe and Farr (2) found marked differences in the topography of deposits formed above and below a critical electrolyte temperature range of 94°-98°C. In order to compare these deposit structures, plating was carried out at 10 ma/cm^2 for 30 min (giving a 6μ thick deposit) at 25° and at 99°C.

Figure 2 is a Berg-Barrett image of the substrate, and the linear striation substructure is seen as light and dark bands. The circular area corresponds to a porosity hole formed in freezing the metal. This feature proved useful as a location mark.

In the image from the deposit formed at 25°C (Fig. 3), the hole may be seen, but there is no evidence of the striation substructure. In contrast, the striation structure has clearly been reproduced in the deposit formed at 99°C (Fig. 4).

It appears therefore that deposits formed above 98°C are epitaxial with the substrate. While Laue spots were still obtainable from the deposit formed at 25°C, the deposit no longer conformed so closely to the structure of the substrate.

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The Mechanism of Electrolytic Rectification

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It has been known for a long time that the system metal/metal oxide/electrolyte, where the metal is Ta, Al, etc. (so-called valve metals), exhibits rectification. When the metal is anodically polarized, there is a "small" current, the leakage current; when the metal is cathodically polarized, a "high" current flows, the forward current.

Various theories, as mentioned in Schmidt's article (1), have been proposed to explain the phenomenon of electrolytic rectification, *viz.*, semiconductor theories; mechanical defect theories: pores, flaws, microfissures; electrochemical theories. A conclusive explanation has not yet been found.

A number of more or less well-known phenomena concerning the electrolytic rectification have been collected below, and on this basis a new theory is proposed (proton current mechanism).

A. On polarizing Ta anodically in an electrolyte an oxide film is formed; its thickness is proportional to the forming potential at constant current density. Subsequent cathodic polarization causes a "high" current flow; hydrogen is developed, and after some time the Ta metal becomes hard and brittle (2).

B. The system Al/Al_2O_3/metal or Ta/Ta_2O_5/metal probably exhibits no rectification in an absolutely dry state. The presence of moisture (H_2O) seems essential for rectification (3).

C. Anodic oxide films, obtained by forming, are not porous if well prepared. With the electron microscope one can detect very few or no pores; furthermore it is known that Al_2O_3 membranes are able to withstand gas pressure differences of 0.14 atm without leakage (1).

D. The system, Ta/Ta_2O_5/evaporated Pt, exhibits a higher conductance in a H_2 atmosphere. Au or Al counterelectrodes do not exhibit this effect (1).

E. It is possible to separate Al_2O_3 films from the underlying Al metal by an excessive H_2 development, *e.g.*, by switching d.c. or a.c. The developed H_2 hardly dissolves in Al at room temperature and acts as a wedge between the Al and the oxide film (4).

These phenomena can be interpreted in terms of the following mechanism:

$-$		$+$
M	M oxide	electrolyte or other proton donor, *e.g.*, H_2O or Pt/H
$e+H^+\rightarrow$	H $\quad H^+\leftarrow$	$\nearrow$
$\leftarrow$	H $\longrightarrow$	$H+H\rightarrow H_2$

When the valve metal is negatively polarized, protons from the electrolyte can diffuse through the oxide film under the influence of the applied field (see above). The latter is considerably smaller than the forming field, and therefore the assumption is made that the mobility of the protons in the oxide is considerably larger than that of the Ta or Al ions. The protons arriving at the metal/metal oxide interface will be neutralized to H atoms.

These H atoms can either dissolve interstitially in the metal (point A) or collect at the interface. The H_2 gas so formed can either diffuse back to the electrolyte or crack the oxide film and disappear as H_2 gas (point E). Point B is also consistent with the suggested mechanism because moisture (H_2O) might act as a source of protons.

The mechanism suggested here differs considerably from the theory based on pores, etc., as proposed by Young (2), Vermilyea (12), and Kleefstra (14). Point C, however, indicates that at least in many cases, there are very few or no pores in the oxide layer (15). It is believed therefore that the mechanism suggested in this paper is better justified.

A further justification for the proposed mechanism can be found in the behavior of the glass electrode which is known to act as a membrane permeable for H^+ ions. It is known that anodic oxide films, obtained by forming at moderate temperatures, are amorphous and glassy. The author is thinking of a parallel with the glass electrode. The diffusion of very small charged particles (protons) is much more probable than the diffusion of uncharged, bigger particles (H atoms) as Schmidt proposes. Moreover, the hypothesis of Schmidt necessitates an electronic current to flow through the oxide to promote the reaction $H^+ + e \rightarrow H$ or $(H_3O)^+ + e \rightarrow H + H_2O$ at the interface oxide/electrolyte. In this case it is also difficult to see why the H_2 should not choose the much easier way of escaping via the liquid electrolyte. It may be remarked that in principle the same theory may be valid under certain conditions for other "small" positive ions, *e.g.*, Na^+. In that case the dehydration energy of the cation must play an important role and acts as an extra barrier in the double layer near the oxide/electrolyte interface.

A difficult point in the aforementioned mechanism was the fact that the "solid" Ta capacitor exhibits rectification even when encased in a "moisture-free" can. In recent literature, however, it is found that pyrolytic MnO_2 contains various amounts of hydrogen (16-19) so that the MnO_2 can act as the proton donor.

There are strong indications that the electrolytic rectification phenomena can be fully explained with the hypothesis of proton conduction through bulk oxide, although mechanical defects may play a certain minor role.

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