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## ON THE MECHANISM OF ELECTROLYTIC RECTIFICATION

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### Summary

It is shown that electrolytic rectification can be considered as a process taking place uniformly across the surface layer.

### Résumé

On démontre, qu'on peut considérer la rectification électrolytique comme un processus qui a lieu uniformément en travers de la surface.

### Zusammenfassung

Es wird gezeigt, daß man die elektrolytische Gleichrichtung als einen Prozess betrachten kann, der gleichmäßig auf der ganzen Oberfläche vor sich geht.

## 1. Introduction

It is well known that, after anodic oxidation of metals like Al and Ta, the system metal/metaloxide/electrolyte shows rectification. However, the origin and seat of this property is unknown. Especially the question whether this rectification is uniform across the surface or is restricted to (many) spots on the surface, is often discussed.

It is the aim of the present paper to show that up till now there are no definite indications for "point rectification". In this discussion we have restricted ourselves to Al-oxide layers.

## 2. Observations on the aluminium surface

(a) A sheet of Al is etched for 3 minutes in hot 5% NaOH and subsequently for 1 minute in cold 4N.H<sub>2</sub>SO<sub>4</sub>. After this a replica is made of the surface and studied in an electron microscope. It is seen (fig. 1) that the surface shows a series of "plateaux" of about 0.1  $\mu$  in diameter. They are also often found in groups together. Moreover, the impure Al (99.5%) does show many more of these spots than the pure Al (99.99%), which shows only a few.

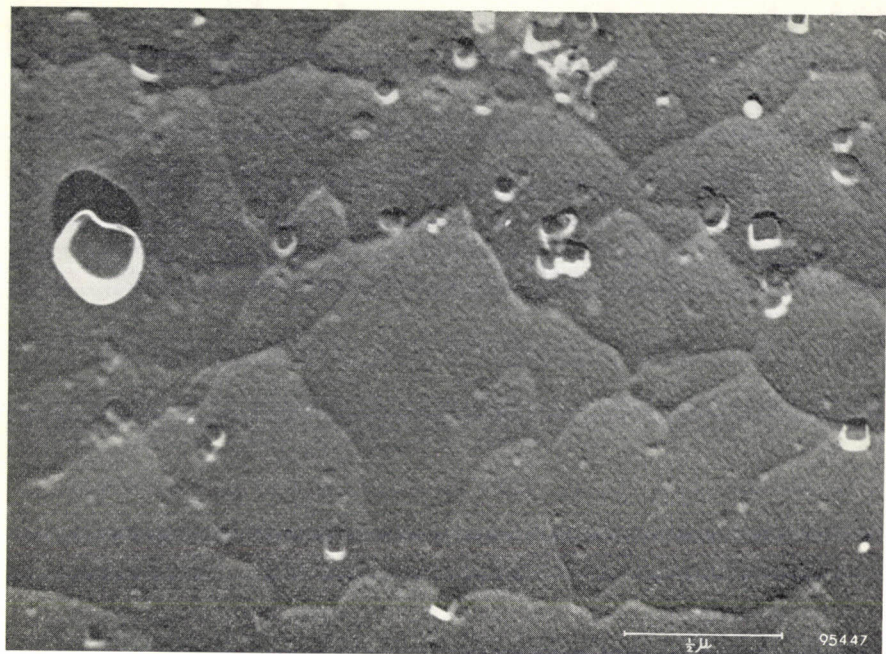


Fig. 1. The replica of an Al surface after etching (Al of 99.5% purity).

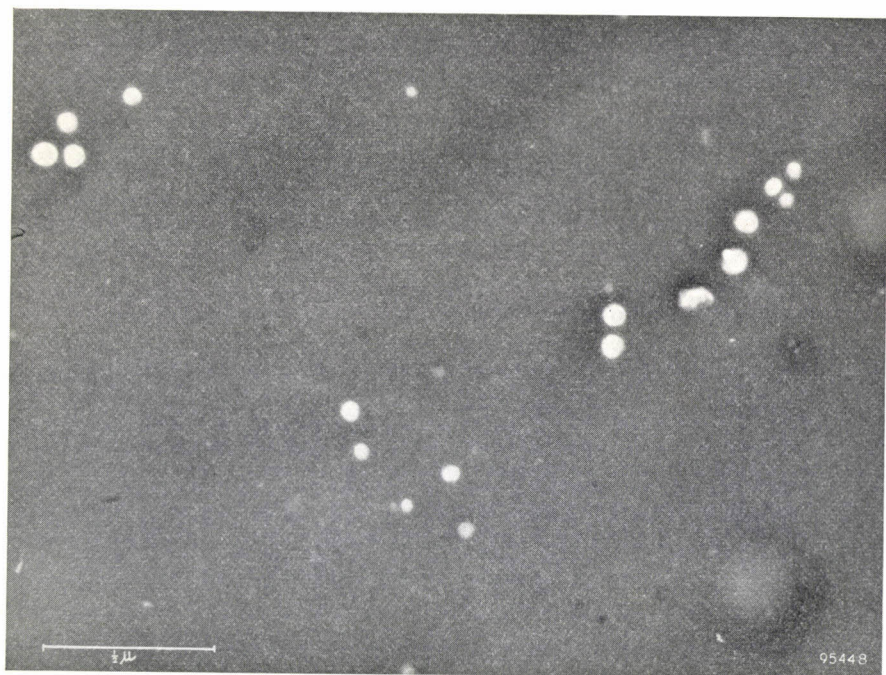


Fig. 2. The Al-oxide layer resulting from anodic oxidation of the surface of fig. 1.

So we are inclined to ascribe these "plateaux" to segregations of impurities in the Al, which are less attacked by the alkaline and acid treatment than the Al atoms.

(b) A sheet of Al, treated as described sub (a), is oxidized anodically. After this the oxide layer is separated from the Al by a methanol-bromium treatment. This oxide layer is also studied under the microscope. In the oxide (fig. 2), a number of holes were observed which show in some respect a strong analogy with the "plateaux" described above. This confirms what could be expected: on the places of the impurities no (or only some) oxide will grow.

(c) Recently <sup>1)</sup>, experiments have been published concerning Al sheets which, after oxidation, were placed in a radio-active gold solution. After a short time (e.g., 30 sec), some activity is found on the Al sheet. As it is not possible that the Au ions exchange with the Al ions of the oxide (in the case of no external voltage), it was suggested that there are "open areas" in the oxide, due to impurities where the Au could be deposited by electrochemical displacement.

At first sight, however, the picture of the active sheet is not the same as given in figs 1 and 2: the active spots are much larger. But taking into account the existence of groups of small spots as well as the limited resolution of the autoradiographs (2 to 3  $\mu$ ), one may say anyhow that there is no contradiction between the experiments. Calculations of the observed activity show that quantitatively the larger spots may consist of a number of small spots.

Concluding this section, we may say that during the growth of the oxide layer weak places or even holes \*) remain where impurities are present in the underlying base metal.

### 3. Does point-contact rectification occur?

If rectification would take place at isolated points and not uniformly across the oxide layer, these points might be correlated with the open spots, as described in the previous section.

This assumption has two consequences:

(a) The current level in both forward and blocking directions will of course be higher with the impure Al as compared with the pure Al (different number of spots). However, the rectification factor (the ratio of the two currents) will be independent of the purity of the Al.

It is difficult to determine this factor experimentally. The forward current is very large and is limited not by the oxide, but by the external

\*) These holes should not be confused with the equally spaced pores that are present in oxide layers formed in oxalic or sulfuric acid baths.

part of the circuit. We tried to measure the current ratio both with a small sheet ( $5 \text{ mm}^2$ ) in "plenty" electrolyte and a small electrolyte contact on an oxidized sheet. The value of the forward current, if only due to the spots of sec. 2, exceeds  $1000 \text{ A/cm}^2$ ! This value is so high that a more uniform current distribution seems likely.

(b) If the contact of the electrolyte with the impurities would cause rectification, it is likely that this would also be observed in the case of a capillary filled with electrolyte, in contact with a sheet of Cu, Fe or Pt. However, in this case rectification is not observed.

So these results do not show any evidence for point-contact rectification.

#### 4. Some remarks

We would like to make a few remarks in relation to a recent article dealing with this subject <sup>2</sup>).

(a) During the forward current, the hydrogen bubbles at the oxide/electrolyte interface originate from quite definite spots of the surface and not at random. After the voltage has been reversed for some time, again the bubbles originate from the same spots. However, also some new places are created and some old places stop bubbling. Now these located "craters" need not be an indication that the current flows through these places only. For it is well known that also at the Pt electrode the bubbles are coming from well-defined places ("active places"), whereas the discharge is uniform. And when these places are masked, new spots come into existence.

Although the spots of the impurities will certainly be favoured points for these "active places", this is no proof that the discharge would not be uniform.

(b) One might think that by scanning the surface with a very thin metal wire <sup>2</sup>), the spots of rectification should be located. But it is well known that by replacing the electrolyte by a metal (e.g., by evaporating this metal onto the oxide), there is often no rectification left <sup>3</sup>). Although the background of this fact is not quite clear, this makes the suggested method doubtful. In fact with scanning no rectification was observed <sup>2</sup>), but this seems not in contradiction with a uniform rectification in the case of the electrolyte electrode.

#### 5. Conclusion

There is no coercive evidence for a rectification mechanism taking place only at small spots on the surface. However, the spots, as found in sec. 2, certainly will contribute to secondary effects, especially to the "leakage" current.

On the other hand, we would like to lay some emphasis on the following facts:

(a) The property of rectification is independent of the treatment of the Al surface and independent of the impurities.

(b) The rectification is macroscopically the same for quite different materials. So also Ta shows electrolytic rectification (after anodic oxidation) where quite different impurities are present, arranged in quite different ways and eliminated differently by different surface treatments. Also we like to mention in this respect that the large absorptivity of Ta for hydrogen atoms will create a situation at the Ta electrode completely different from that of Al.

Concluding we may say that the electrolytic rectification can still be considered as a uniform process, although this process itself may not be known exactly.

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