

mechanism of organic molecules for TiO₂ electrode. All other detailed studies are being carried out.

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ELECTROCHEMICAL SURFACE MODIFICATION OF ALUMINUM-SURFACE PROFILING BY INTERFEROMETRY

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Preliminary
Communication

Abstract – The surface analysis using interferometry studies clearly indicates that the oxidation cycling at high frequency at aluminum electrode in the 0.1M NaClO₄ containing 10 mM sodium tetraphenylborate solution yields selective dissolution of faces other than (111) by forming pyramidal shape voids that is not due to the simultaneous dissolution and redeposition as in the case of Pt. It is also confirmed that surface smoothing and flattening on the aluminum surface is due to flattening process and the formation of voids are due to electrochemical dissolution.

Key words: aluminum, interferometry, faceting, and hydrophobic additive

INTRODUCTION

The status on reconstructed electrode surfaces has been summarised, placing emphasis on the in-situ scanning microscopy studies in a recent review by Kolb [1]. The author also describes the conditions under which reconstructed surfaces are stable in solution and describes about the potential induced reconstruction and the transition between reconstructed and unreconstructed surfaces. The modification of electrode surface has been done by employing different techniques, namely: sputter and annealing in UHV, Flame annealing and potential-induced reconstruction. The most widely used one is the repetitive oxidation/reduction cycling in a suitable electrolyte in high frequency. Due to this potential cycling, there is an increase in roughness and

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also leading to preferential orientation of the polycrystalline surface or preferred dissolution. This aspect has been exploited by several authors [2-6] and it is explained in detail in the recent review article of Kolb [1]. Arvia et al [3] exploited this essentially for pc-platinum and pc-gold, but however this media and methods are not suitable for metals like aluminum, because the aluminum dissolution terminates due to passivation. In order to avoid this passive film formation, hydrophobic substances like tetraphenylborate anion were used [7]. This anion is expected to increase the rate of dissolution / passivation steps by promoting the strong chemisorptive interaction between aluminum surface and aqueous layer [8, 9]. So, In this context, it has been demonstrated in a previous paper the possibility of reconstruction of aluminum surface using tetraphenylborate anion in neutral aqueous solutions containing ClO_4^- [2].

EXPERIMENTAL

The samples were prepared as previously [2]. Neutral 0.1M sodium perchlorate solutions were used for the electrochemical treatment of aluminum of 99.999% purity (Goodfellow, UK). The pulsing potential was chosen from the cyclic voltammetric experiments of the mechanically polished electrode in a 0.1M sodium perchlorate solution. A conventional three-electrode cell was employed for the CV and pulsing experiments. The pulse was initiated from -0.900 V vs SCE (OCP) to dissolve aluminum anodically and brought back to OCP to effect only aluminum dissolution. The pulse time duration for this cycling was 100 ms each for a total period of 15 min. Three electrodes were prepared for the analysis. i) Mechanically polished aluminum substrate using 1/0, 2/0, 3/0 and 4/0 emery papers (Disc of area 0.3 cm^2) subjected to the potential pulse treatment in 0.1M sodium perchlorate solution ii) mechanically polished substrate subjected to the potential pulse treatment in 0.1M sodium

perchlorate solution containing 10mM sodium tetraphenyl borate and iii) mechanically polished aluminum substrate was just kept for 30 min. in 0.1M sodium perchlorate solution containing 10mM sodium tetraphenyl borate. All solutions were prepared with reagent grade chemicals (supplied by Merck) and Millipore filtered deionised water with a resistivity of $18\text{ M}\Omega$ and were deoxygenated by bubbling with Argon for 30 min. before starting each experiment.

The samples were examined through three-dimensional imaging interferometric surface structure analyzer (ZYGO New View 100, US). The interferometric surface analysis microscope uses scanning light interferometry to image test part surfaces and provide surface structure analysis without contacting the surface. Measurement is three-dimensional. A piezo scanner performs vertical measurements normal to the surface. Lateral measurements in the plane of the surface are performed by calculating the pixel size from the field of view of the objective in use. Lateral resolution of 50 nm is obtained with the powerful objective. With this, New View 100 depths up to $100\text{ }\mu\text{m}$ with 0.1 nm resolutions and 0.3 nm RMS repeatability are imaged independent of the objective magnification.

RESULTS AND DISCUSSION

Immediately after preparing the electrode the interferograms were taken in order to have understanding of the surface. Fig .1a shows the interferogram of the aluminum electrode treated with 0.1M NaClO_4 solutions. In order to reliably characterise the samples by interferometry, a good survey of images was taken in different regions of each sample. It is clear from the three-dimensional figure that the electrode surface has undergone uniform dissolution. The average roughness was calculated to be 341 nm and the surface to valley height was found to be $2.97\text{ }\mu\text{m}$. It is also calculated that the root-mean square deviational of

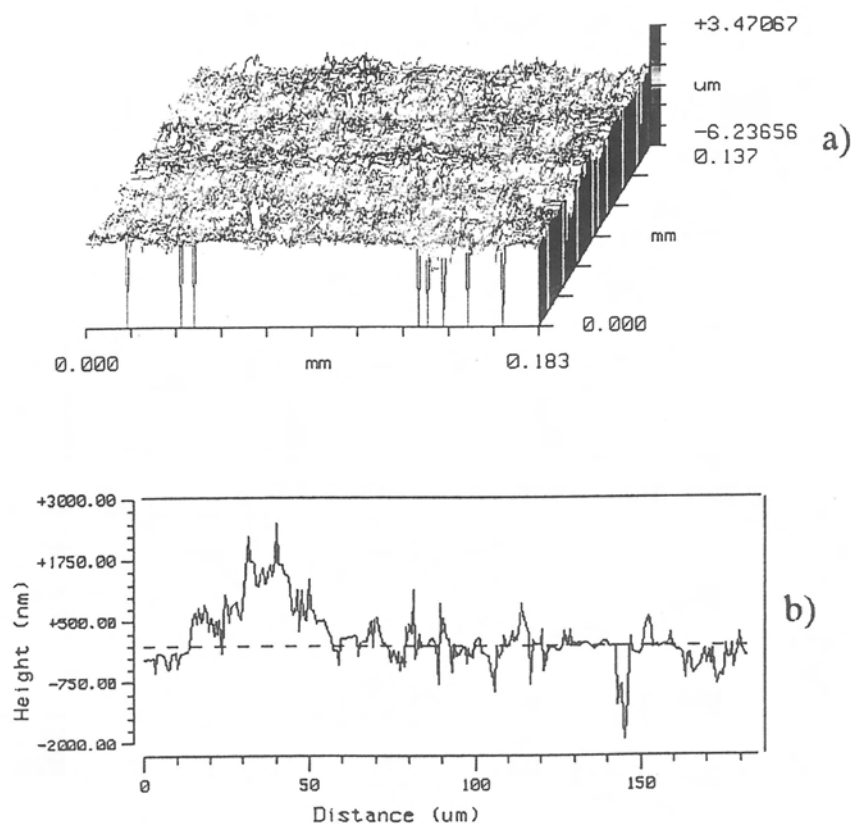


Fig.1. a) Interferogram and b) profile of the aluminum electrode electrochemically treated in 0.1 M NaClO₄ solution

all the points from a plane fit to the test part surface is 448 nm. It is known that in the case of aluminum at anodic potentials there are two competing reactions taking place, namely: oxide formation and aluminum dissolution. The CV can explain about the current reduction due to the formation of Al₂O₃ on treating with 0.1 M NaClO₄ solution (see Fig. 1b in [2]). This may be because the rate of formation of oxide is higher and is responsible for the reduction in current. The profile of the Fig. 1a is presented in Fig. 1b, that also confirms the presence of block oxide (Al₂O₃) on the surface with the height of about 1.75 μm and it is clear from the figure that this oxide is not uniform through out the surface. Anodic dissolution of aluminum metal occurs at appreciable rates in solution containing aggressive anions, particularly in chloride [8], or in strong alkaline electrolytes [9]. So it is clear from the above results that neutral solutions containing ClO₄⁻ are not as aggressive as others and provides some way for the formation of passive oxide.

Fig. 2a shows the 3D figure of the aluminum electrode kept for 30 min. in 0.1M NaClO₄ containing 10mM tetraphenyl borate solution. The full survey of the electrode shows that the surface has become smoother due to the presence of tetraphenylborate anion. The average roughness is calculated to be 291 nm and the peak to valley height is 1.03 μm. It is also calculated that the root-mean-square deviation of all the points from a plane fit to the test part surface is 378 nm. It is clear both from figure and profile in Fig.2b that the aluminum undergoes uniform corrosion or smoothing and flattening of the roughed surface. This may be due to the tetragonal structure of the large area of tetraphenyl borate molecule (=121 Å²) [10] and also a hydrophobic substance is expected to reduce the strong chemisorptive interaction between water and metal surface [11]. The driving force for the smoothing is the reduction in surface energy. It is worth to mention here that, according to Gibbs-Thomson equation [12], the chemical potential of an atom on a curved surface will be

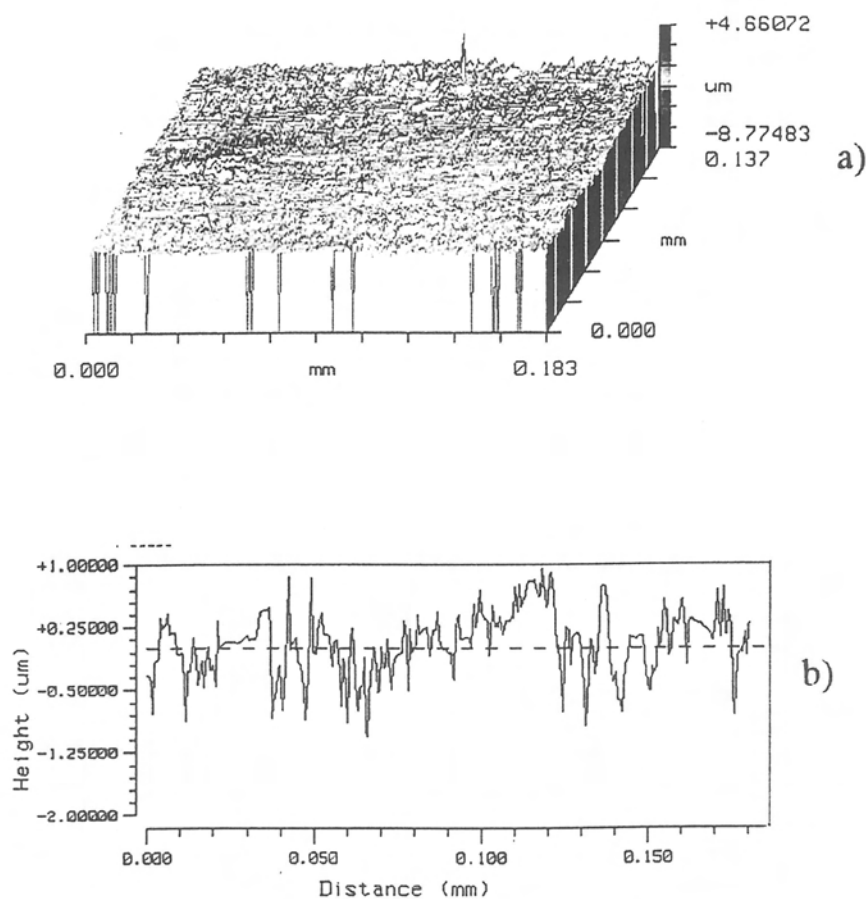


Fig.2. a) Interferogram and b) profile of the aluminum electrode immersed in 0.1M NaClO₄ containing 10mM tetraphenylborate solution for 30 minutes.

different from that on a flat surface. So this difference causes material to redistribute in a direction of annihilating such difference until equilibrium is established. Therefore, in this process, hills will reduce their height and valleys will be filled [13, 14].

Fig 3a shows the 3D figure of the aluminum electrode electrochemically treated with 0.1M NaClO₄ containing 10mM tetraphenylborate solution. The full survey of the electrode shows that the surface has become smoother because of the corrosion in the edges of the electrode. The average roughness was calculated to be 2.21μm (including the valleys) and the peak to valley height is 23.2 μm. It is also calculated that the root-mean-square deviation of all the points from a plane fit to the test part surface is 3.02 μm. In the presence of tetraphenyl borate anion in the competing reaction at anodic bias, the rate of formation of oxide is comparatively slower than dissolution of aluminum and also the borate ion facilitates the etching at the corner of the defects. This etching creates small (111) faces[1]. This may be further dissolved vertically to form pyramidal shape (111) face. This pyramidal shape of depth with stepped sides is clear from the profile presented in Fig. 3a and Fig 4a-c confirming the dissolution of other faces than (111). Comparing the Figs. 2a and 3a, it is worth to mention that in both cases the chemical etching is taking place and this pyramidal shape of depth is present only when doing the electrochemical cycling. It is also noted that under the experimental conditions maintained in this work, the tetraphenylborate anion does not undergo any redox transformation leading to electro active species [15, 16]. In addition, no decomposition of BPh₄⁻ is envisaged due to the neutral condition of the solutions employed in this work [16].

The surface analysis using interferometry studies gives the following informations. The oxidation/reduction cycling at high frequency at aluminum electrode in the 0.1M NaClO₄ containing 10mM tetraphenyl borate solution

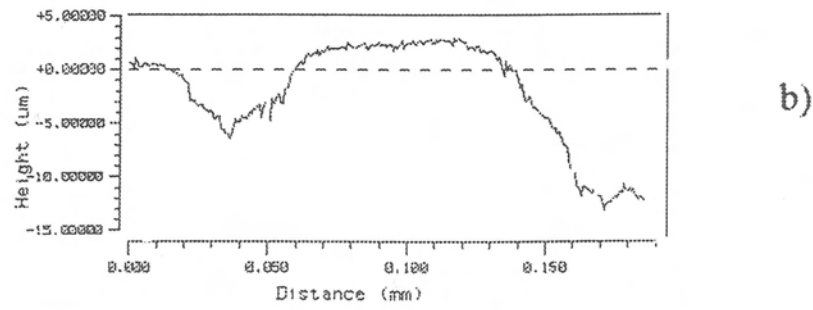
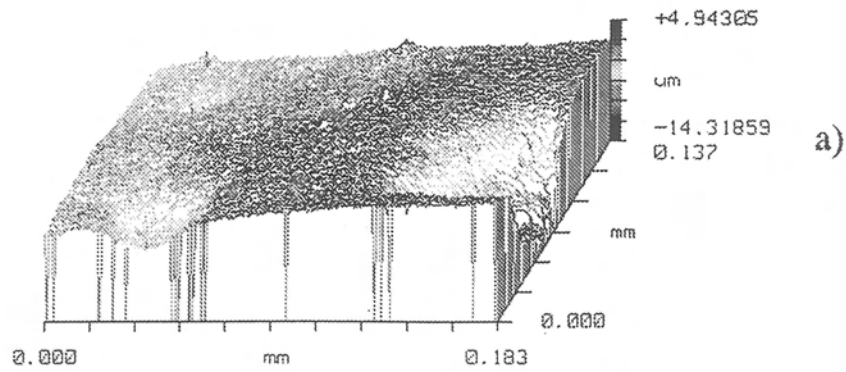


Fig.3. a) Interferogram and b) profile of the aluminum electrode electrochemically treated in 0.1 M NaClO₄ containing 10mM tetraphenylborate solution.

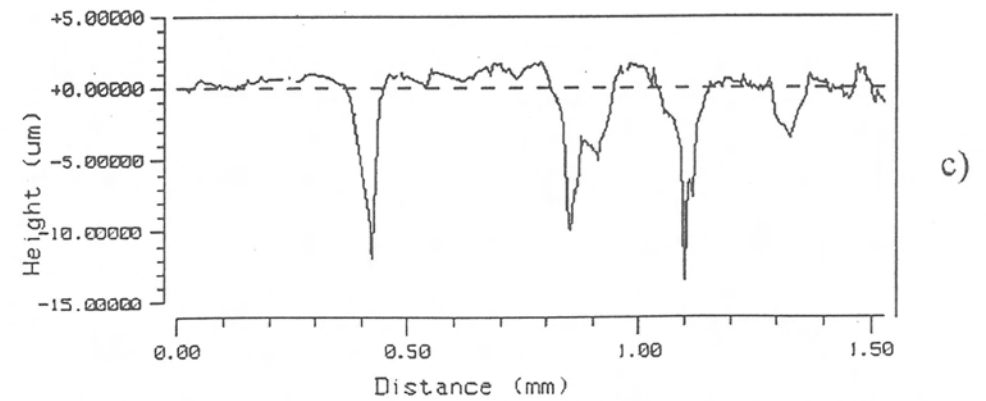
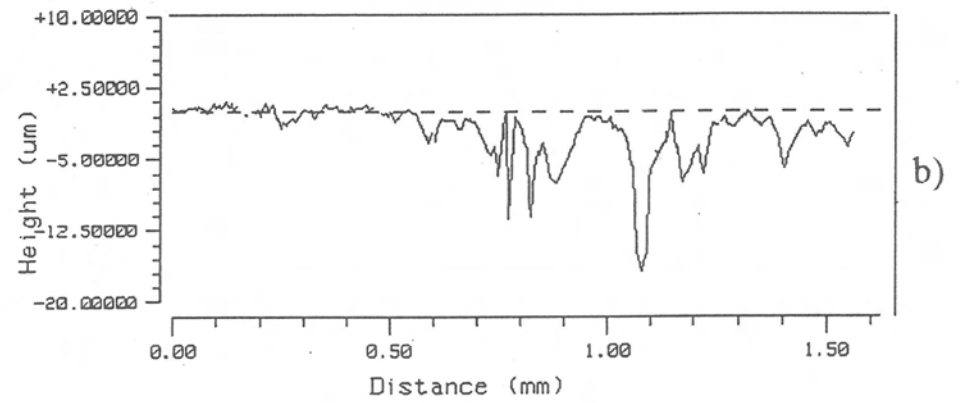
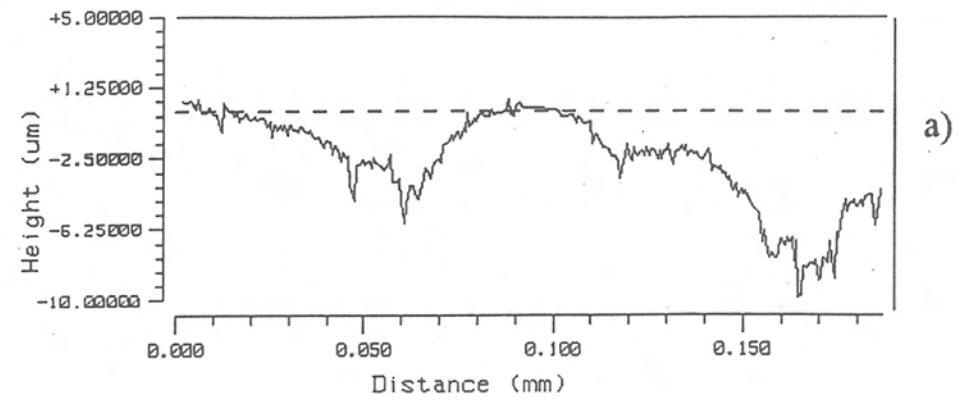


Fig.4a-c. Profiles at various places and for different lengths of the aluminum electrode electrochemically treated in 0.1 M NaClO₄ containing 10 mM tetraphenylborate solutions.

yields selective dissolution of faces other than (111) by forming pyramidal shape voids that is not due to the simultaneous dissolution and redeposition as in the case of Pt. It is also confirmed that surface smoothing on the aluminum surface is taking place here, which is due to the flattening process and the formation of voids are due to electrochemical dissolution.

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