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Confocal Microscopy Study and Corrosion Process: the Al-(HF, HNO_3, HCl) System

Séverine Mathis and Michel Coster

LERMAT, URA CNRS 1317, ISMRA, 6 bd Maréchal Juin, 14050 Caen, France

Résumé. — Les mesures électrochimiques ne donnent aucune information sur la morphologie de la corrosion. Dans cet article, nous proposons d'utiliser un microscope confocal et l'analyse d'images pour suivre le processus de corrosion de l'aluminium par un mélange d'acides. Pour faire l'analyse, les outils de morphologie mathématique en niveaux de gris ont été utilisés. Divers paramètres de rugosité et divers paramètres topologiques ont été utilisés. Ils ont permis de mettre en évidence que le processus de corrosion est gouverné par deux phénomènes opposés : la minimisation de l'énergie du système et la dépendance de la vitesse de corrosion avec les hétérogénéités du matériau (joints de grains, réseaux de dislocations, ...).

Abstract. — Classical electro-chemical measurements do not give quantitative information on the morphology of corrosion process. In this paper, a complementary way to study the corrosion process using a confocal microscope and image analysis is proposed. By this way, the corrosion of aluminium by a mixture of acids was studied. To perform this analysis, morphological tools dedicated to grey tone images were used. The corrosion process was studied by several roughness and topological parameters. Their evolutions during corrosion process show that two opposite phenomena must be taken into account in this corrosion process: the minimisation of the energy and the dependence of the corrosion rate with the heterogeneities of the material (grains boundaries, dislocations networks, ...).

Introduction

Electro-chemistry measurements are able to give some global information about the corrosion, but it does not give any quantitative information on morphological aspects of corrosion. The corrosion will change a mirror polished surface into a rough one. A morphological study of those rough surfaces on a micrometer scale should give some further information about the corrosion mechanism. To study these corroded surfaces, a confocal microscope Zeiss LSM 310 in the reflection mode was used to obtain topographic images.

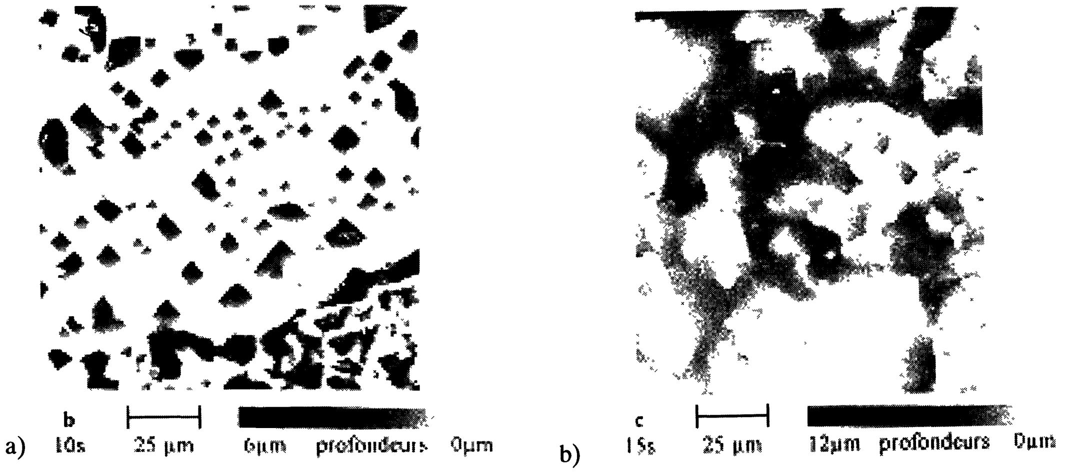

Fig. 1. — a) Topography of etched aluminium after 10 s. b) Topography of etched aluminium after 15 s.

Materials and Experiments

Small and thin polycrystalline aluminium bars were first polished to obtain a mirror polished surface, then etched a few seconds by an acid mixture (50% HCl, 47% HNO_3, 3% HF). Some images of acid corroded aluminium are shown in Figure 1 for different corrosion time. Figures 1a and 1b indicate clearly that the corrosion process begins through the formation of etch pits with a well defined geometrical shape. The square shape (Fig. 1a) shows that the crystallographic orientation of the grain surface is close to $\{001\}$. For each corrosion time, acquisition, pre-treatment and measurements were performed on 25 images of the same metallographic section.

Topographic Acquisition and Elimination of Artefacts Zones

Topographic data are calculated from series of confocal images in the reflection mode. Images are taken at regularly spaced altitudes from the top to the bottom of the sample field. One can get quite a good depth discrimination thanks to the laser scanning system, the pinhole and the high numerical aperture of the objective lens. In the "topographic mode" of the confocal microscope, a sample surface point appears in the same position in each confocal image of the series, with more or less brightness depending on the distance to the focal plane. The image where the point is the brightest indicates for which stage-plate position the point was in the focal plane: therefore, the altitude is known (topographic image). However a very low value of this maximum intensity (intensity image) corresponds to a pixel without good information and can belong to an artefact zone. Artefacts can be classified in our preliminary study, in two cases:

- when the slope is steep the light is reflected away from the detector and the altitude is badly computed (Fig. 2a),
- when there is a narrow and deep valley, most of the light does not reach the bottom of the valley; a part of the reflected light does not reach the detector (Fig. 2b).

These artefact zones can be easily eliminated by a simple threshold.

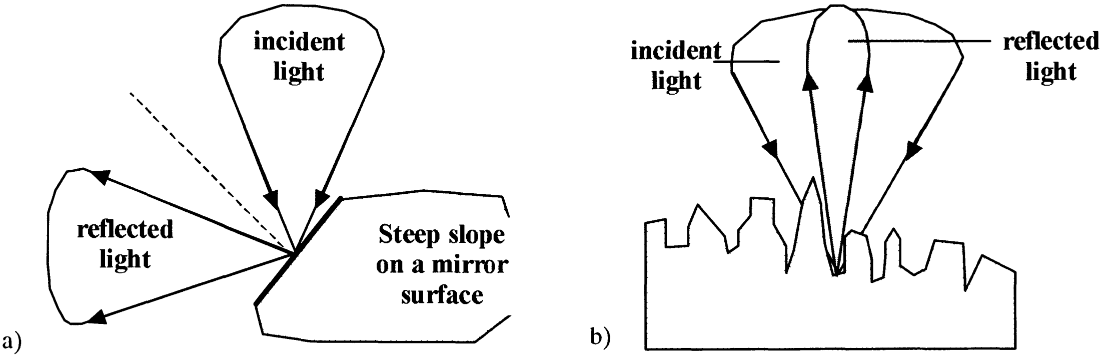

Fig. 2. — The origin of artefacts on confocal topographies. a) Reflection problem leading to a lack of signal. b) Lack of signal due to a large numerical aperture and a narrow valley.

Pre-Treatment for Altitude Correction

Some parts of the aluminium surface remain untouched at the beginning of the etching (Fig. 1a). Thanks to the non etched zones, one has a reference level, which is important to obtain an absolute topography at the beginning of the corrosion process. At first, a pre-treatment is applied to the topographies in order to correct the very slight slope of the sample on the microscope. In the initial topography, the flat places whose gradient is nil are selected, and the other places are set to grey level 0 to be eliminated. One can get almost the reference image with a large closing. A small opening is also useful to filter some small defects or dust traces. The difference between the reference image and the initial image gives a precise and absolute topography. This pre-treatment is valid when there are enough non corroded surfaces. But when a very large closing of the flat places is not enough to cover all the other places, the reference level is the maximum altitude in the initial topography. The quality of the topographic confocal images is very good and some other classical filters seems to be useless.

Morphological Parameters and Results

In a mathematical sense, a topographic image is equivalent to a grey tone image where a grey level corresponds to an altitude. For the grey tone images, a large range of morphological parameters is possible [1-3]. Only, the more significant parameters for our corrosion study have been chosen.

MEAN ETCHING DEPTH MEASUREMENTS AND CORROSION RATE. — To obtain a comparison between image analysis measurements and a physical corrosion measure, the corrosion rate was calculated physically from weighting and geometrically by image analysis. The difference between weights before and after etching is the weight of solved aluminium. By this method, the mean depth etching rate would be 0.20 μm/s. The depth etching over all the image can be also obtained from the volume of aluminium removed from etching divided by the area of the support of the image. The mean value obtained of corrosion rate is around 0.14 μm/s according to topography analysis. These two methods give approximatively the same value. The value obtained by weighting is greater because two reasons. The corrosion rate is faster on the edges of the samples (these zones are not taken into account in image analysis). Since both uniform and localized

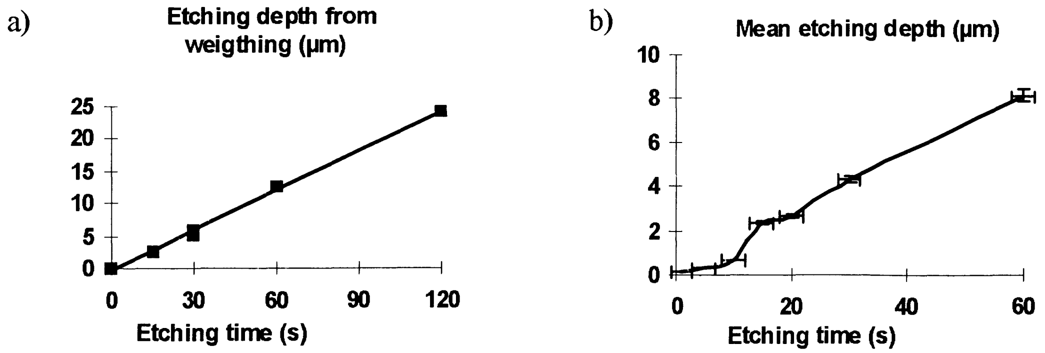

Fig. 3. — Etching rates according to weithings or image analysis.

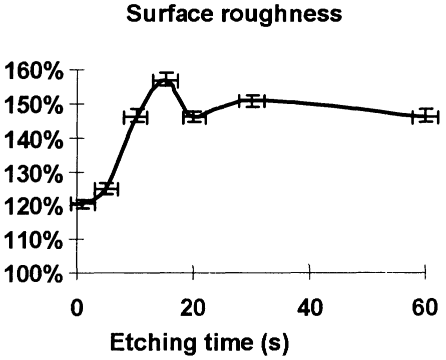

Fig. 4. — Evolution of surface roughness as a function of etching time.

corrosion processes are superposed, the reference levels of topographic measurements after longer testing times do not correspond exactly to that of the non-etched surface.

Each parameter was applied to the different etched aluminium samples. The mean etching depths from weighting or from image analysis are shown in Figure 3. The etching rate seems to be constant in the etched places whereas it is not over all the aluminium surface. The change of slope of the curve presented in Figure 3b seems be correlated to a stepwise evolution of the surface morphology: regular etching pits until $t = 10$ s (Fig. 1a), then rapid smoothing of localized corrosion sites after $t = 10$ s (Fig. 1b).

SURFACE ROUGHNESS. — The surface roughness R_A is the ratio of the upper surface of the aluminium sample to its projected area. There are many ways to calculate the upper surface on a digital topography [4-6]. According to Hénault [5, 6], a triangular approximation of the upper surface is the best method. It was decided to use this method to calculate the surface roughness.

The surface roughness oscillates with the etching time (Fig. 4). From these oscillations, one can deduce that there are two opposite phenomena: one is smoothing the aluminium surface, the other makes it rougher. The corrosion indeed tends to erase peaks, which smoothes the aluminium surface, whereas it also creates new hollows on the emerging dislocation points.

Until the testing time of 10 s, the localized corrosion takes place through formation of regular etch pits (Fig. 1a). Since the crystallographic orientation of the corroded surface is $\{001\}$ the roughness of an individual localized corrosion site with a pyramidal shape can be easily calculated. It is close to 170% and independent on the pit size supposing that no localized dissolution take

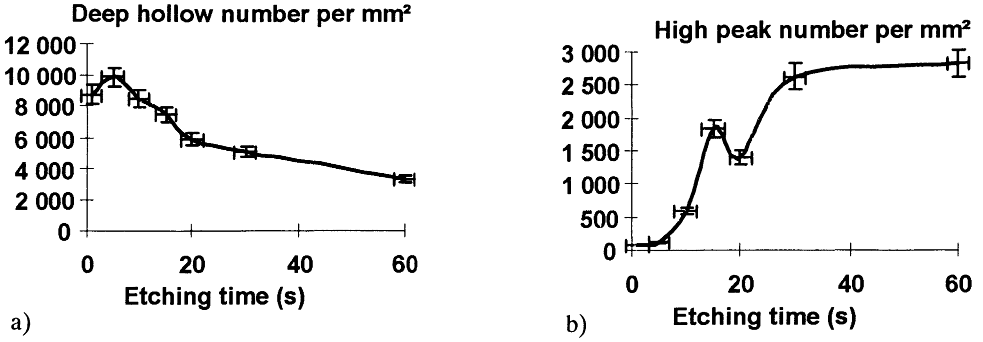

Fig. 5. — a) Evolution of specific deep hollow number as a function of etching time. b) Evolution of specific high peak number as a function of etching time.

place on the pit walls. The reduction of the surface roughness correlates well with microscopical observations.

PEAK AND HOLLOW NUMBERS. — The third parameter used is the number of maxima or minima per projected area unit on the topographies. The maxima correspond to the peaks and the minima correspond to hollows. But when the images are a little noisy or if we are not interested in very small peaks and hollows, only high peaks or deep hollows can be counted. This is the reason why the h-minima and the h-maxima transforms were used [7].

To obtain the h-minima, the function $f + h$, where h is a constant, must be eroded until idempotence in a geodesic way over the function f using a flat structuring element. So one obtains a new function g and the difference between g and h gives the hollows "deeper than h".

The h-maxima transform, h-max(f) was also used to count peaks higher than h or $h >$ maxima. These h-max(f) are obtained by the geodesic dilation of $f - h$ under f until idempotence and difference with the initial image. The maxima of h-max(h) are showing the peaks higher than h on function f. Finally, the numbers of maxima, minima, $h >$ maxima or $h >$ minima per projected area unit can be counted over all the aluminium surface or only over etched places on the aluminium surface.

For any morphological transform, it is better to apply the measure mask theorem [8], but it is impossible or very difficult for h-minima and h-maxima transforms since we do not know the maximum necessary erosion or dilation size. One also has to be careful when counting minima and maxima: it is like counting binary objects (binary connected sets): there is no perfect method. The best way found is to use a kind of shell correction [9, 10] in order to count only once objects which are touching the image frames.

These hollows and peaks can be also counted (Figs. 5a and 5b). The hollows appear in the topographies if they are at least deeper than 0.1 μm. The deep hollows, deeper than 1.6 μm, are computed from the h-minima transform. On all the aluminium surface, the number of hollows oscillates because some new hollows always appear but they also merge. As the hollows enlarge until they merge, the number of hollows per etched area unit is decreasing until most of the surface is etched.

As the hollows, the peaks appearing in the topographies are higher than 0.1 μm, and the deep peaks are higher than 1.6 μm (they are calculated from the h-maxima transform where $h = 1.6$ μm). Peaks are appearing when some hollows are merging. All the peaks are on the etched surface. The number of peaks per aluminium area unit is increasing with the etching time like the etched specific surface whereas the number of peaks per etched area unit oscillates.

After sixty seconds of etching, the specific etched surface is almost 100%: therefore the numbers of peaks or hollows deep or not per aluminium area unit are nearly equal to the numbers per etched area unit. Moreover the numbers of peaks and the numbers of hollows tend to stabilize at the same value: the hollow or peak numbers seem to stabilize around 100 000 and the deep hollow and high peak numbers seem to stabilize around 3 000/mm^2.

Conclusion

In this paper, a new way is proposed to study corrosion by the mean of confocal microscopy. The electrochemical methods and simple weight loss do not give information about the regular or not regular morphological evolution during corrosion process. Three phenomena are indeed involved in the corrosion process:

- the increasing roughness due to nucleation and growth of etching pits related to crystalline defects (dislocation networks and grain boundaries),
- uniform dissolution of metal which does not modify the morphology,
- the surface smoothing according to thermodynamical laws (minimization of energy). Fortunately, there are not many artefacts in topographies of polished, then corroded samples. Since there are some zones without localized corrosion on the material, there is a "reference level" and several measurements are possible. Topography analysis offers some detailed and reliable information about corrosion. It should be interesting to apply this method to other investigations in the field of corrosion.

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