Structural Disintegration of Al 2024 Rolled Plates in a Marine Environment: Effect of Morphological Parameters of the Microstructure

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1. Introduction

The exfoliation corrosion (EC) is a well known degradation mode of several aluminum alloys, strongly dependent on aging conditions and on morphological parameters of the microstructure. It occurs exclusively in microstructures composed of plate-like or fibrous grains, typical for rolled plates and sheets. It consists in an intense corrosion (inter- or transgranular) with propagation paths parallel to the rolling surface, followed by the material disintegration through 'exfoliation' (Fig. 1).

Fig. 1. Exfoliation corrosion as visible on a section of an Al 2024 T351 rolled plate after the immersion test according to ASTM G34.

The sensibility of a material to the exfoliation corrosion is evaluated according to ASTM G34 through a simple immersion test followed by optical examination of the sample surface [1]. However, while this standardized testing procedure takes indirectly into account the amount of the material degradation in the bulk, it is not always adequate to reproduce the materials behavior in service conditions. A general mechanism of the exfoliation corrosion does not exist, but in many cases EC can be considered as a result of the synergy between chemical (localized corrosion) and mechanical (stresses induced by corrosion products) factors [2,3]. From this point of view, the phenomenon belongs to the category of corrosion-deformation interactions [4]. Intergranular stresses required to separate an individual surface grain from the polycrystalline sample were estimated in 1980s close to 5MPa [5] but controversies remain if exfoliation can really be considered

as a 'cracking' process or if it simply results from the expansion of corrosion products acting against a grain already physically separated from the bulk.

In the present paper, a classical Al 2024 T351 alloy, known for its sensibility to exfoliation corrosion, was investigated after natural exposition in a marine environment during 1 to12 months, more adequate to the conditions of outdoor service than those of the G34 immersion test. In particular, it was attempted to establish a relationship between the grain shape and orientation with respect to the surface exposed and the risk of exfoliation corrosion. Finally, a simple exfoliation mechanism taking into account the geometry of grains and mechanical conditions along dissolved grain boundaries is proposed to explain experimental data.

2. Materials and experimental conditions

The study has been carried out on samples issued from a rolled plate, 35mm thick, of a commercial Al 2024 T351 alloy. The microstructure is composed of plate shaped grains, oriented parallel with respect to the L-LT plane (Fig. 2). The linear grain dimensions are approximately 300μm, 100μm and 20μm, respectively for L, LT and ST directions. Samples have been exposed in a marine environment during 1 to 12 months at the French Corrosion Institute in Brest. After visual surface examination, observations on a LT-ST cross section, according to Fig. 2, have been carried out by optical microscopy.
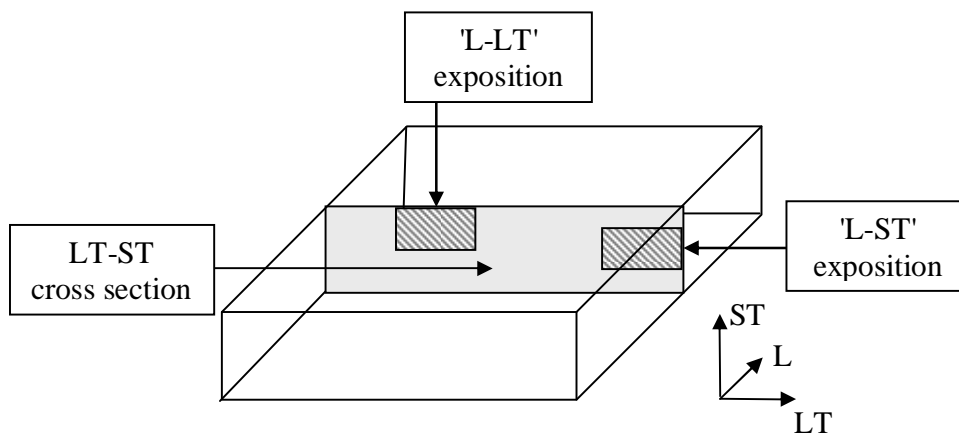

Fig. 2. Orientation of samples for corrosion examination.

3. Localized corrosion

3.1. Surface aspects

Observations after one month of exposition reveal the presence of less brilliant regions (corrosion initiation zones ?), independent on the surface orientation. The density of such zones does not exceed 5 per 100 sq. millimeter. After six months, blisters are clearly visible on the L-LT plane. Their density is equal to that of

initiation zones observed after the exposition of one month. The coalescence of blisters on the L-LT plane produces the characteristic aspect of the metal surface, well known from the G34 immersion test, while two other surfaces (ST-LT and L-ST) are not affected by any localized attack, as compared with the situation observed after the exposition of one month.

3.2. Localized corrosion in the bulk

Fig. 3 shows the aspect of the LT-ST cross section after exposition of the L-ST surface (Fig. 2) during one and six months. In both cases, intergranular corrosion, starting from few intersections of grain boundaries with the L-ST surface, can be observed. After one month, the maximal penetration depth reaches roughly 300µm and no measurable evolution takes place when the exposition continues until the total duration of six months.
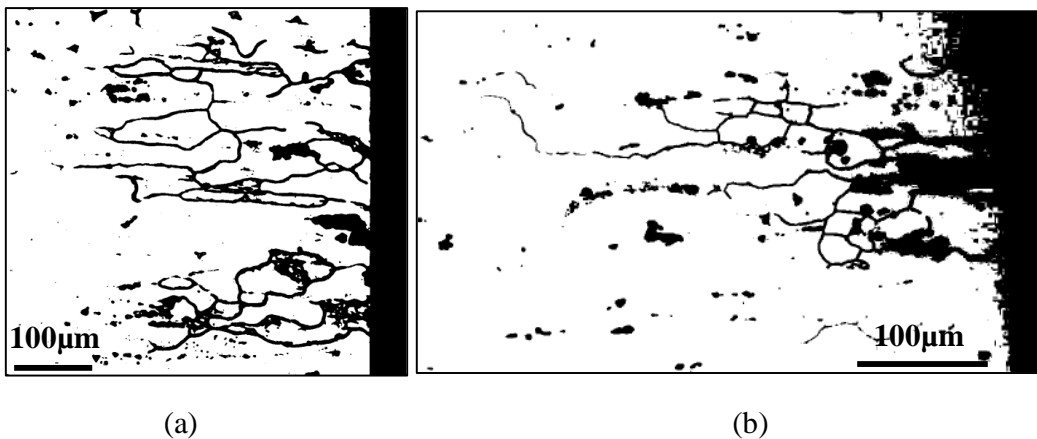

(a)   (b)

Fig. 3. Intergranular corrosion on the LT-ST cross section (L-ST plane exposed) after (a) 1 month and (b) 6 months exposition.

A radically different corrosion behavior has been observed on the LT-ST cross section exposed from the L-LT plane. After one month exposition, intergranular corrosion has progressed (Fig. 4) over roughly the same distance as in the case described above but, because of the orientation of grains with respect to the exposed surface, the penetration depth (perpendicular to the surface exposed) does not exceed 100µm. However, the main difference concerns the beginning of blister formation through displacement of thin grains perpendicularly to the sample surface. Corrosive environment can thus penetrate inside the material and reach freshly exposed grain boundaries as indicated by arrows in Fig. 4.

Observations carried out on the same cross section after six (Fig. 5a) and twelve (Fig. 5b) months confirm the decisive role of the initial grain displacement with respect to the corrosion kinetics. The width of the corroded layer reaches 1.5mm after six months and nearly 3mm after one year. Therefore the progression is nearly linear versus time which contrasts with the observations reported in Fig. 3

for which the 'ordinary' intergranular corrosion reached its maximal penetration after only one month and did not progress during further exposition.

Fig. 4. Intergranular corrosion and first stage of blister formation on the LT-ST cross section exposed during 1 month from the L-LT plane.
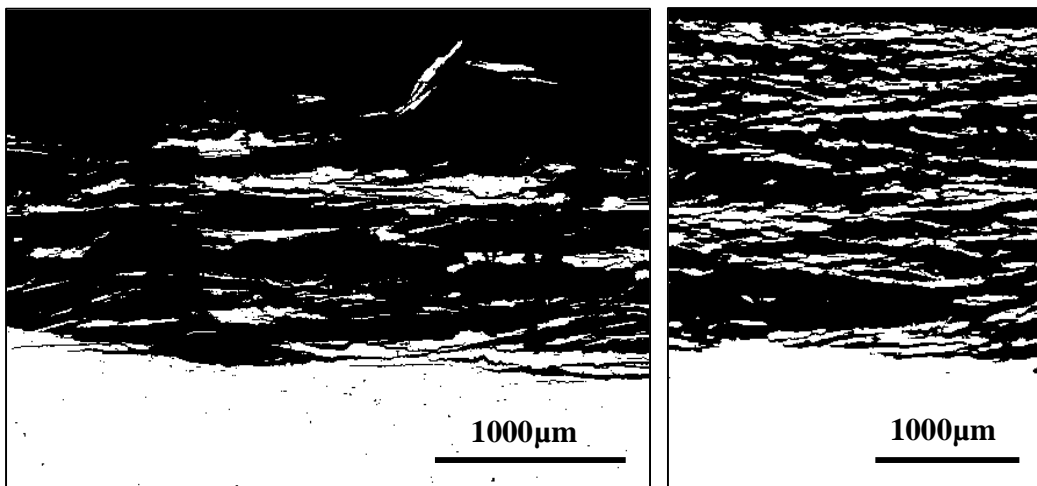
(a)

(b)

Fig. 5. Effect of exfoliation corrosion on the microstructure integrity as observed on the LT-ST cross section after expositions from the L-LT plane during six (a) and twelve (b) months.

4. Relationship between exfoliation corrosion and microstructural parameters

Observations reported above give precious information about the mechanisms of the exfoliation corrosion and about some kinetic aspects of damage. Firstly, intergranular corrosion is undoubtedly the basic damage mechanism. Secondly, the penetration of the 'pure' intergranular corrosion, i.e. non followed by exfoliation, stops at depths close to 300µm and it does not affect the microstructure integrity when the exposition is continued. The intergranular corrosion evolution can be easily represented with the help of a simple 2D geometrical model of the microstructure (Fig. 6).

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It is assumed, for simplicity, that intergranular corrosion starts from a single grain boundary intersection with the metal surface. Corrosion progresses along the boundary until the nearest triple point is reached. According to observations, corrosion follows then two newly exposed boundaries and the path bifurcation takes place at every new triple point (equal probability of all possible intergranular corrosion paths).

The second basic assumption concerns the intergranular corrosion rate. The simplest way is to assume that corrosion rate remains constant versus time. That means that the environment responsible for grain boundary dissolution is 'injected' into the bulk at a constant rate. At every triple point, corrosion path splits and the local corrosion rate is divided by factor two. Consequently, after the nth bifurcation, the local corrosion rate V_n is:

$$V_n = \frac{V_0}{2^n} \qquad (1)$$

where V_0 is the corrosion rate along the boundary emerging at the surface.

In Fig. 6, a 2D microstructure composed of grains with the average shape factor 'l/h' equal to five is represented. Intergranular corrosion is supposed to initiate from two emerging boundaries, one parallel to the long axis of grains ('L-ST' exposition) and one parallel to the short one ('L-LT' exposition), simulating the real situations observed on the LT-ST cross section (Fig. 2).
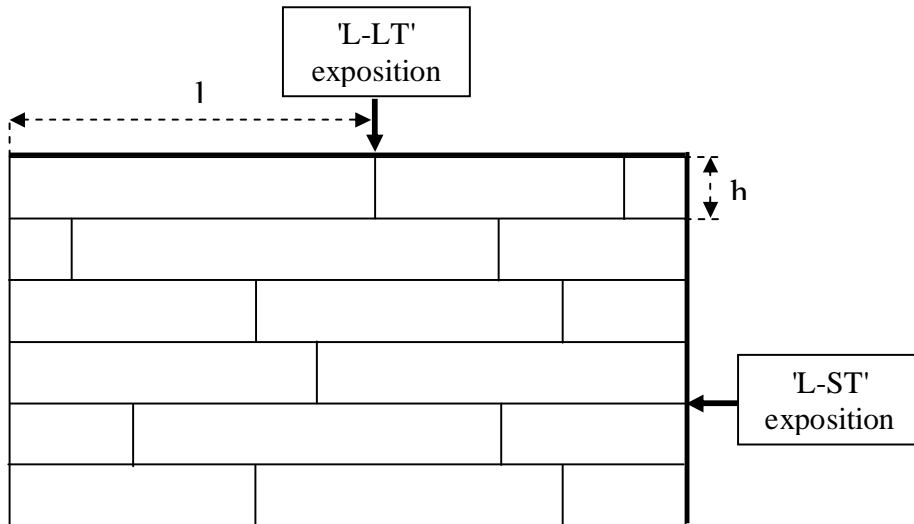

Fig. 6. Two dimensional model microstructure with the average shape factor 'l/h' equal to five. Arrows indicate grain boundaries along which corrosion initiates.

According to Eq. 1, intergranular corrosion rate drops by 50 percent when corrosion path bifurcates at triple points. The consequence is a rapid decrease of

the global penetration distance from the free surface and, in the practice, the propagation arrest.

In Fig. 7, the theoretical evolution of intergranular corrosion on the LT-ST cross section according to Fig. 2 has been represented for exposition times of 1, 5 and 15 (arbitrary units). The shapes of the affected zones are indicated. They correspond qualitatively to those observed experimentally (Fig. 3,4).
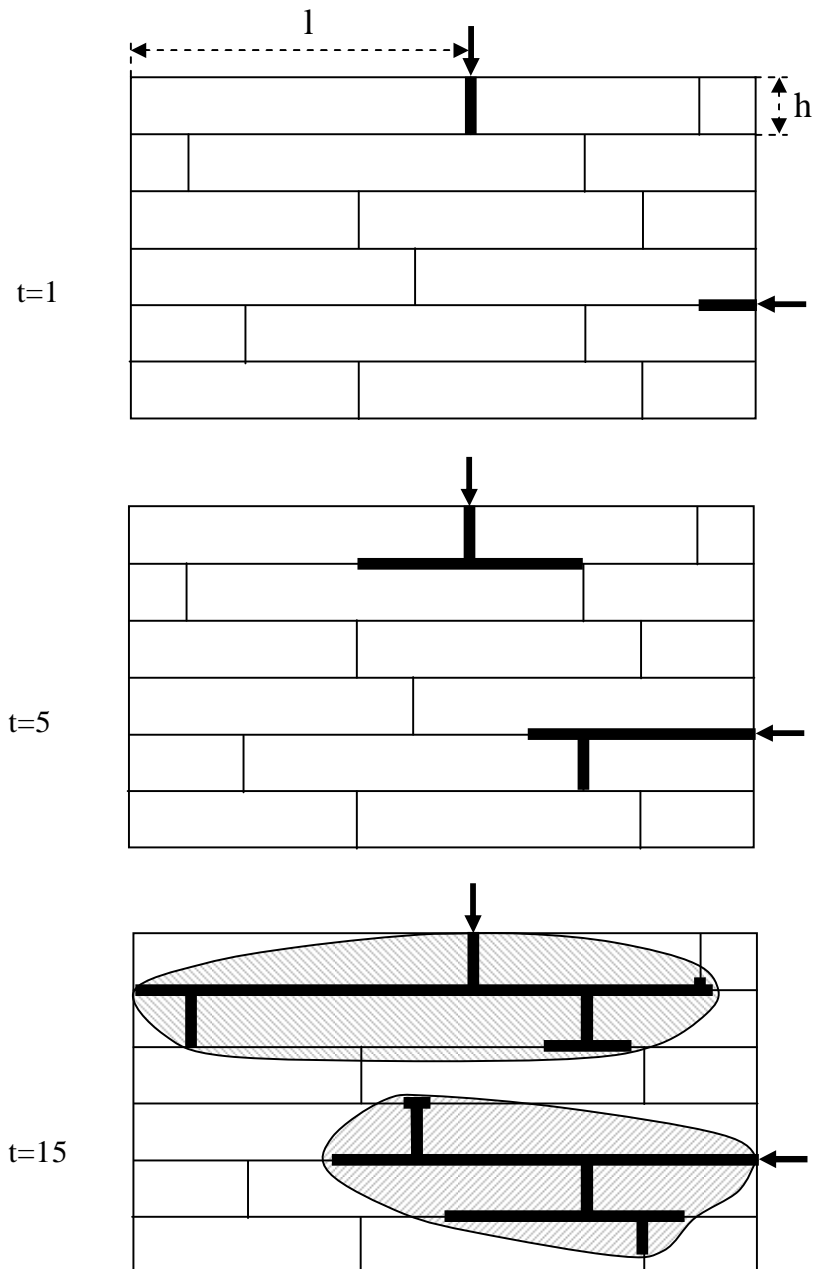

Fig. 7. Simulated evolution of intergranular corrosion on the simulated LT-ST cross section (arbitrary time units).

According to Fig. 7, grain exfoliation is only likely to occur when corrosion is initiated from the sample surface parallel to the long axis of grains. Segments of the intergranular corrosion path between consecutive triple points are a linear function of the shape factor of grains. Consequently, long segments of corroded grain boundaries are filled with corrosion products whose expansion can help to remove surface grains from their initial position and enable the penetration of the corrosive environment into the free space created (cf. Fig. 4). The process can thus be periodically reactivated which explains a nearly linear evolution of the exfoliation corrosion versus time (Fig. 5) while the intregranular corrosion rate rapidly drops to zero, when no exfoliation is possible (Fig. 3).

5. Estimation of the intergranular pressure required for exfoliation

According to the schematic representation presented in the previous section, intergranular corrosion will degenerate towards exfoliation if grains from the surface layer are deformed or displaced enabling the corrosive environment to penetrate along previous boundaries and reactivating locally the initial corrosion rate. This elementary event is illustrated in Fig. 8. A section parallel to the short axis of an elliptic blister shows two grains with the shape factor of roughly 10, deformed through the internal pressure of corrosion products along dissolved grain boundaries. The vertical grain displacement 'f' as seen in Fig. 8 can result both from a local force P applied at their extremities and from a uniform stress q/b acting on the grain surface, 'b' being the grain dimension along the direction parallel to the long axis of the blister (Fig. 8):

$$f = \frac{4Pl^3}{Ebh^3} + \frac{3ql^4}{2Ebh^3} \tag{2}$$

In the present case, the only contribution to be taken into account is that of the pressure 'q', so that Eq. 2 reduces to a very simple form:

$$f = \frac{3ql^4}{2Ebh^3} \tag{3}$$

Consequently, for given morphological parameters of the microstructure (l, b, h), it is possible to calculate the intergranular stress 'q' required to induce the grain flexion 'f' (Fig. 9). For the configuration presented in Fig. 8, this intergranular stress is close to 0.5 MPa which is roughly 10 times lower from the Robinson's estimation [5]. This result is not really surprising if one takes into account that the mechanism proposed in the present approach does not involve mechanical failure but only a deformation of grains previously separated from the bulk through intergranular corrosion.
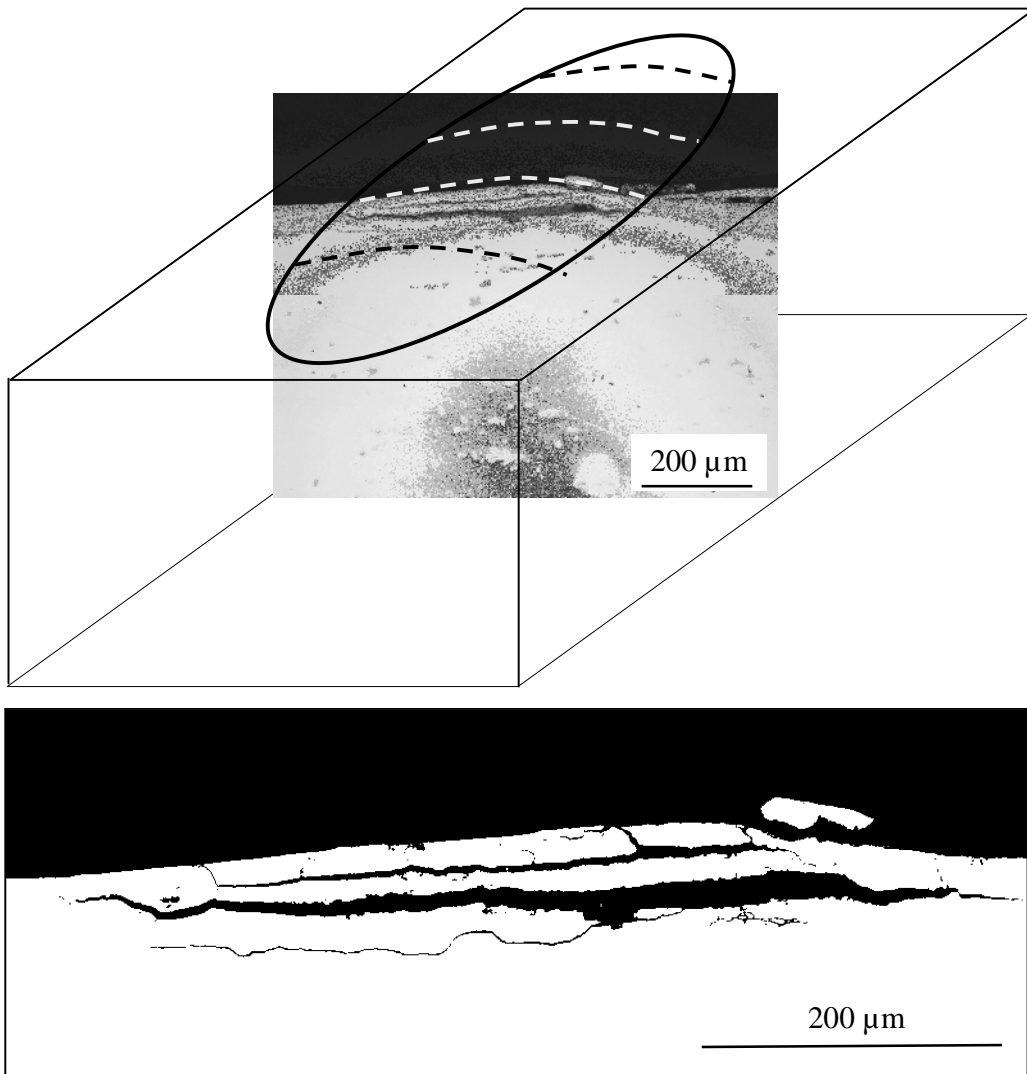
Fig. 8. Initial stage of exfoliation in a 2024T351 alloy exposed during 1 month
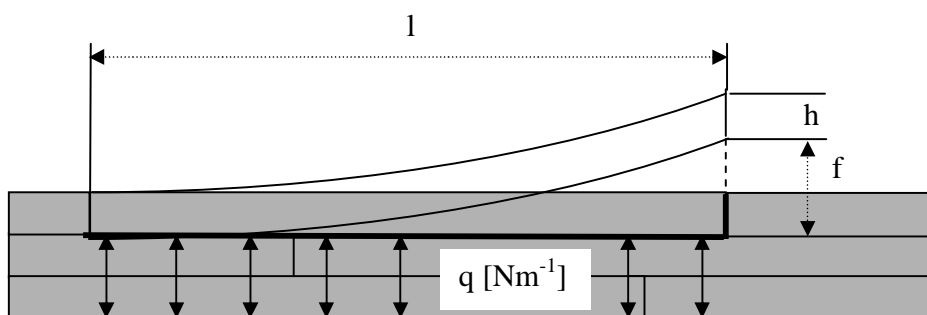in a marine environment.

Fig. 9. Grain flexion induced by the pressure of corrosion products along
a dissolved grain boundary.

The principal advantage of the approach presented above is therefore to estimate the pressure of corrosion products 'q' between adjacent grains. This gives a possibility to investigate for which grain geometry ('l/h' ratio) a critical grain flexion 'f', necessary to allow the penetration of the corrosive environment in the intergranular zone, will occur.

6. Conclusions

Al 2024T3 rolled plates exposed in a marine environment are heavily affected by the exfoliation corrosion on the surface parallel to the rolling direction. The same microstructure with the long axis of grains perpendicular to the exposed surface is only sensible to the 'ordinary' intergranular corrosion with a maximal penetration depth of roughly 300µm and nearly no further evolution after expositions longer than one month.

Exfoliation corrosion can be considered as a degenerated form of intergranular corrosion induced by a combination of chemical (grain boundary dissolution) and mechanical (grain deformation and/or displacement) factors.

A simple model of intergranular corrosion taking into account the reduction of the propagation rate at triple points correctly reproduces experimental corrosion patterns observed on sample sections.

The intergranular pressure required to deform flat surface grains with the shape factor close to 10 has been estimated close to 0.5MPa. Consequently, predictive simulations of the exfoliation corrosion can be realized with fixed threshold values for intergranular pressure and grain displacement and for different intergranular corrosion rates.

Acknowledgements

References

[1] ASTM G34 - 01(2007) Standard Test Method for Exfoliation Corrosion Susceptibility in 2XXX and 7XXX Series Aluminum Alloys (EXCO Test)

[2] F. Bellenger, Etude et contrôle de la corrosion feuilletante des alliages d'aluminium 2024 et 7449 par bruit électrochimique et émission acoustique. Analyse microstructurale et caractérisation de l'endommagement, PhD Thesis, Institut National des Sciences Appliquées de Lyon, France, 2002

[3] C. Kuntz-Laguerre, Contribution à l'étude de la compréhension des phénomènes chimiques engendrant la corrosion feuilletante des alliages d'aluminium et de la quantification de cette corrosion, PhD Thesis, Université Paris VI, France, 1997

[4] T. Magnin, Advances in Corrosion-Deformation Interactions, Trans Tech Publications, Zürich, 1996

[5] M.J. Robinson, Mathematical Modelling of Exfoliation Corrosion in High Strength Aluminum Alloys, Corrosion Science 22 (8) (1982) 775-790