STUDY OF DEGRADATION MECHANISMS OF BLACK ANODIC FILMS IN SIMULATED SPACE ENVIRONMENT

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ABSTRACT

Black anodic films are used on aluminium alloys in space applications to provide specific thermo-optical properties to the surface. During the process, thermal and/or residual stresses can lead to crazing of the film in particular conditions.
After thermal cycling performed to simulate the space environment, cases of film flaking have been observed. This constitutes potential risks for the satellite lifetime.
Peel-test and scratch-test have been used to evaluate the evolution of the adhesion during ageing. For example, we showed that this phenomenon is due to crack propagation occurring at the beginning of ageing.
A finite element model has then been developed to study more accurately the propagation mode of these cracks. Thermal stresses are likely to propagate cracks through the film in pure opening mode. When cracks are long enough, thermal stresses can generate propagation parallel to the interface. This would result in the decrease of the measured adhesion with a possibility of flaking.

1. INTRODUCTION

In the space vacuum, thermal exchanges of a satellite with its environment are only radiative. Surface treatments are often used in space applications to provide specific thermo-optical characteristics to materials [1, 2] and thus, to passively manage thermal control. Black inorganic anodized aluminium alloys are then used for their high solar absorptivity and normal emissivity (α_s>0.93; ε_n>0.9), [3-5]. In addition, those black coatings are especially suitable near optical instruments to avoid stray lights. Moreover, the use of inorganic dyes limits risks of contaminating the spacecraft by outgassing.

With the successive passages of a satellite in the shadow of the Earth in orbit, a satellite is constantly exposed to thermal cycling under vacuum. The temperatures can typically vary between -140°C and 140°C. Many cases of flaking of black anodic films have been observed after thermal cycles carried out to simulate the space environment [3]. Only anodic films on aluminium alloys from series 2XXX and 7XXX are affected by this anomaly. Actually, in orbit, such particles could contaminate instruments of the satellite and reduce its lifetime.

The black anodizing process and the influence of its parameters on the film morphology were studied in a previous paper [6]. It has especially been shown that the Young modulus of black anodic films is directly depending on the initial porosity and thus, on the anodizing temperature. A temperature range varying from 5±0.5°C to 25±0.5°C is actually leading to increasing porosities from 10±2% to 50±4% and a decreasing Young modulus from 77±3GPa to less than 10GPa.
In this context, the aim of this paper is to understand the mechanisms leading to flaking occurring during thermal cycling. Two types of black anodic films were realised with anodizing temperatures of 20°C or 25°C. Indeed, cases of flaking were observed on samples anodised at ambient temperature.
Those samples were first submitted to thermal cycling and the evolution of their adhesion on the aluminium alloy substrate was then evaluated by two methods: peel and scratch-tests. The influence of the cycling conditions (temperatures, number of cycles) on films behaviour was particularly studied.
A finite element model was developed to more accurately understand the mechanisms of crack propagation during thermal cycling leading to flaking. The influence of the hot temperatures (>20°C) and cold ones (<20°C) on the stress state in the film was particularly investigated.

2. EXPERIMENTAL PROCEDURE

The substrate material was the 7175T7351 aluminium alloy, often used in space industry. Its chemical composition in weight percent is: 1.62%Cu, 0.12%Fe, 2.42%Mg, 0.01%Mn, 0.06%Si, 5.75%Zn, 0.041%Ti, 0.21%Cr and Al the remainder.

2.1 Black anodizing process

The process of black anodizing used followed the ESA Standard [7] for spacecraft design involving four main consecutive steps: surface pretreatments, anodizing, coloring and sealing. Samples were rinsed with distilled water after each step.
The alloy sheet (3x20x40mm) was degreased with ethanol and then etched in Na_2CO_3 and Na_3PO_4 aqueous mixed solution for 5min at 93°C and neutralized in aqueous HNO_3 for 3min at room temperature.
The aluminium sheet was used as anode and a lead plate as counter-electrode in the electrochemical cell. The anodizing was run for 60min in the galvanostatic mode (Ja=1.2±0.1A/dm²) using a sulfuric acid solution (150g/L) thermally regulated. The electrolyte temperature is not clearly defined in the specification and is generally the room one. Two different electrolyte temperatures were then used: 20°C and 25°C resulting in oxide films with initial porosities of 40% and 50% respectively [3].
The anodized part was colored by precipitation of black cobalt sulphide (CoS) in the pores [8]. It consists in an immersion in two successive baths: firstly for 15min. in a solution of cobalt acetate (200g/L) regulated at 43±2°C, and then for 10min in a bath of ammonium hydrosulphide (30g/L) at room temperature.
The sealing step occurred for 25min in a bath regulated at 98±2°C and made up of nickel acetate (NiCH3COO, 4H2O) and boric acid (5g/L both).

2.2 Thermal cycling

Space environment has been simulated in an environmental chamber Sun Electronic System EC11. Thermal cycles were performed in a nitrogenous atmosphere between -80°C and 80°C. A large number of parts of a satellite are in this temperature range in space applications. The heating and cooling speed are 10°C per minute with dwell times of 5 minutes. Each cycle starts by the heating of the samples at 80°C before cooling.

2.3 Adhesion measurement

The peel-test was first used to evaluate adhesion of the films. A 2cm width aluminium tape was stuck on films. A tensile test device was used to remove the tape with a constant speed of 500 mm/s. the removal force is perpendicular to the surface of the film. If any particle is detached from the film, the sample is considered as failed.

The adhesion of the films was also evaluated using a scratch-test device (CSM Revetest instrument) with a diamond stylus (Rockwell, 200µm radius tip). Scratch-tests were configured with an increasing normal load (loading speed: 30N/min; advance speed: 5mm/min).
The resulting scratch-print of 5mm length was observed by scanning electron microscopy (SEM Philips XL 30 ESEM) to determine the corresponding normal load. The failure criterion was the flaking of the black anodic film along the scratch. A critical load was defined as the minimum normal load applied on the stylus leading to the lateral flaking of the black anodic film. Given values are averages of six different scratches on each sample.

2.4 Finite element model

A finite element simulation was used to evaluate mechanical behavior of a thin film on its substrate. SAMCEF was used to perform isotropic thermo-elastic calculations with 2-dimensional plane strain hypotheses. The geometry used was a substrate (thickness of 3 mm) with an anodic film of 20 µm. Different geometries of cracks in the film have been used and will be described below. Mesh size has been validated by comparing K_I with theoretical values in the simple case of a straight crack perpendicular to the surface.

Materials
The mechanical properties of the substrate are well known (E_s = 72 GPa, ν_s = 0.33, α_s = 23.4 $10^{-6}K^{-1}$). The properties of black anodic films were studied in a previous paper [6] and are assumed to be (ν_f = 0.28, α_f = 13 $10^{-6}K^{-1}$). The young modulus range simulated is 10 GPa / 77 GPa and covers a porosity range of 10% / 50%. The young modulus of those two types of samples experimentally aged was difficult to accurately evaluate by nanoindentation but seems a bit lower than 10 GPa [6].

Loadings
The loading is only thermal, constant and uniform. The temperature chosen are either -80°C or 80°C while the reference temperature of the system is 20°C. All stresses in the model are then due to differential thermal dilatations between the film and the substrate.

3. RESULTS AND DISCUSSION

3.1 Characterisation of the films before ageing

The thickness of the films is approximately 20µm. SEM observations of the black films presented on Fig.1 show the presence of microcracks. The difference of coefficients of thermal expansion between the film and the substrate lead to the crazing of the film during the sealing step at 98±2°C [9, 10]. In addition Liu et al. [11] showed on films isolated from their substrates that the precipitation occurring during the sealing step can induce internal stresses leading to the formation of cracks.

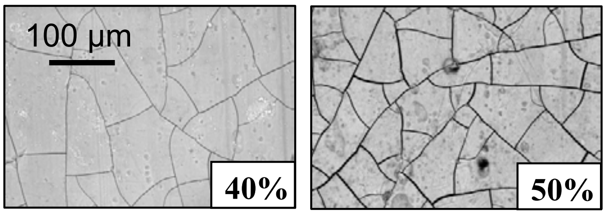

Fig.1. SEM surface observations of two black anodic films with initial porosities of 40% and 50%

The cracks are wider, and then probably deeper [10], on the samples with 50% of initial porosity. This is explained by the decrease of the limit tensile stress of films when the porosity is increasing especially for porosities higher than 30% [9].

Before ageing, in spite of this crazing, peel-tests were successful on both types of samples: no particle was detached by the tape. There is no anomaly detected at this step. The normal load measured by scratch-test is then about 20 N and 17 N for the initial porosities of 40% and 50% respectively.

3.2 Adhesion after thermal cycling

The adhesion of those two types of black anodic films was measured after cycles between -80°C and 80°C.

Tab.1. Results of peel-tests after cycles between -80°C and 80°C successful (/) or failed (**X**)

Initial porosity	Number of cycles							
	Ref	1	3	5	10	20	50	100
40%	/	/	**X**	/	/	/	**X**	/
50%	/	**X**	**X**	**X**	**X**	**X**	**X**	**X**

The results of peel-tests performed after ageing are presented in Tab1. Whatever the number of cycles, particles were detached by the tape from samples with 50% initial porosity (Fig.2). Tests performed on the other type of anodic films are successful except after 3 and 50 cycles where several particles (< 1 cm^{-2}) where detached.

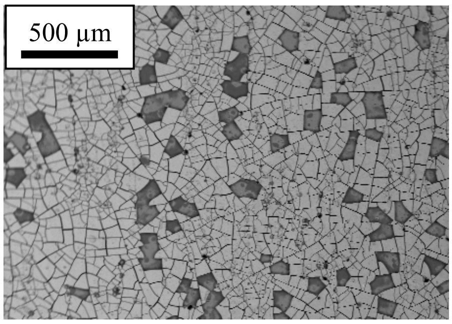

Fig.2. Surface SEM observation of a black anodic film after a failed peel-test

These observations are coherent with scratch-tests results. The adhesion of films with 40% of initial porosity is not affected by this ageing, whatever the number of cycles performed (Fig.3). Nevertheless, a decrease of the adhesion is detected on the other type of samples as soon as the first cycles.

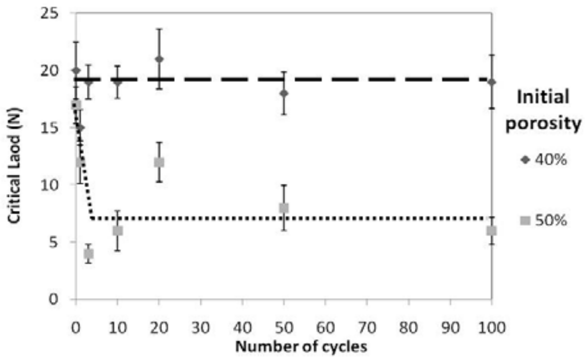

Fig.3. Critical load evolution with the number of thermal cycling performed between -80°C and 80°C

The decrease of adhesion during thermal cycling is associated to crack propagation under stresses. Two types of stresses can be identified:

- First, the coefficient of thermal expansion of anodic films has been evaluated to 13.10^{-6} K^{-1} [12, 13] while the aluminium alloy's one is about 23.4.10^{-6} K^{-1}. This difference of thermal expansion results in tensile stresses in the film when T > 20°C and compressive ones when T < 20°C.
- Secondly, a dehydration of the film may occur during thermal cycling. It may partially relax the internal compressive stresses of the film due to hydration during the sealing step [14].

These stresses may be able to cause the growth of cracks, reducing the load to apply to pull off particles. The difference of behaviour between the two films can be attributed to their difference of limit tensile stress. The cracking resistance is lower in the film with the highest initial porosity [9]. Actually, there is crack propagation if its stress intensity factor (K) becomes higher than the critical stress intensity factor (K_c). K_c is only depending on the materials but difficult to evaluate in the case of anodic films.

3.3 Model of crack growth through the film

The SEM observations of the fractures induced by peel-test or scratch-test coupled with EDX analysis show that the fractures are cohesive in the film. Actually, the anodizing is an electrochemical conversion of the alloy surface. The interface between the film and the substrate has always been considered strong [15].
A finite element simulation has been used to understand the crack growth mechanisms within the film.

Geometry
A 2-D model of the cross-section of a thin film (20 µm) on its substrate (3 mm) before ageing has been created. The influence of a straight crack perpendicular to the surface with a width of 1 µm and a length varying from 9 to 18 µm on the stress state was observed (Fig4).

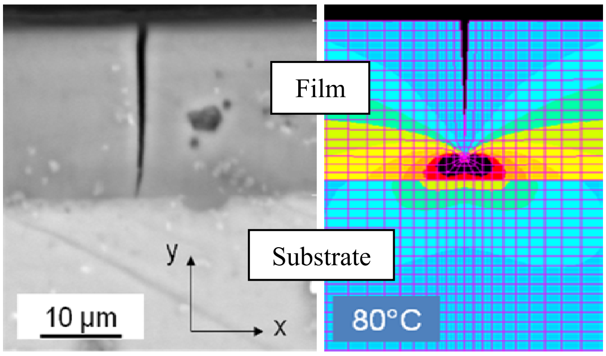

Fig.4. Geometry of the crack in the numerical model (on the right, visualisation of σ_{xx}) compared with a crack observed by SEM on a black anodic film with 40% of initial porosity before ageing (on the left)

Model exploitation
Heating the sample at 80°C generates tensile thermal stresses in the film depending of its young modulus. The crack is then solicited in pure opening mode (Mode I). The evolution of K_I with the young modulus is given on Fig.5 for different crack lengths.

The strains of the film are imposed by the substrate. Thus, an increase of the film's Young modulus results in higher stresses. When the young modulus is close to the substrate's one (72 GPa), the stress intensity factor (SIF) is increasing with the length of the crack as it is the case in an homogenous material.

When the modulus of the film is much lower, the stress intensity factor becomes independent of the crack length. This can be associated to a screen effect of the substrate. When the crack approaches the interface, strains are blocked by the more rigid substrate. That limits the increase of the SIF with the length of the crack.

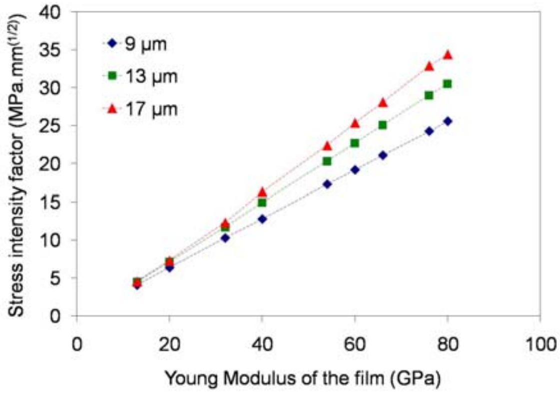

Fig.5. Evolution of the stress intensity of the crack at 80°C with the young modulus of the film for different crack lengths

Whatever the modulus of the film, cracks perpendicular to the surface can grow under thermal stresses for temperatures higher than 20°C.

Lower temperatures than 20°C result in a stress intensity factor equal to zero; compressive stresses close the crack.

3.4 Model of crack growth parallel to the interface

A crack, parallel to the interface may propagate to generate flaking. A numerical model was built to study the mechanisms of growth of these cracks. They can be initiated by the presence of bubbles or defects in the anodic films.

Geometry
A kinked crack was modelled with a varying depth as presented on Fig6. The width of the crack is 1µm and we have shown that the radius of curvature in the kinked part of the crack has no influence on the stress state near the crack tip, in the area used to calculate the stress intensity factor.

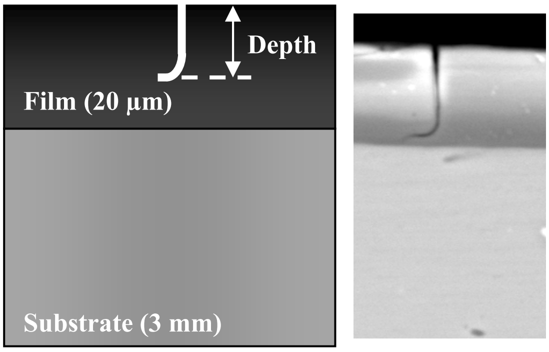

Fig.6. Model (on the left) of the geometry of a kinked crack in a film compared with a SEM cross-section observation of a film with 40% of initial porosity (on the right)

Model exploitation

The differential thermal expansions are generating tensile stresses in anodic films at 80°C. The presence of a kinked part is locally modifying the stress state. Tensile stresses are present on one side of the crack while compressive ones are on the other side (Fig.7).

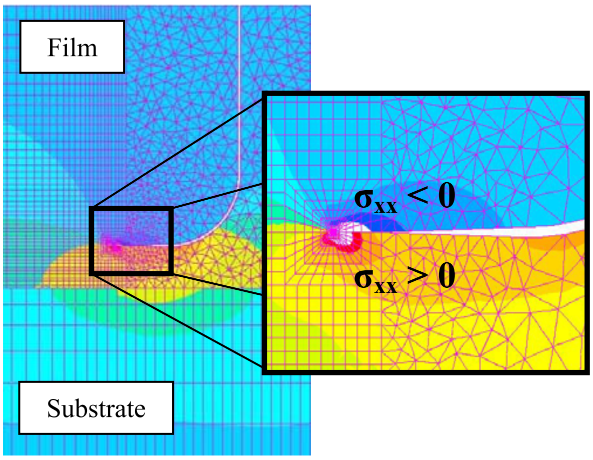

Fig.7. Visualisation of σ_{xx} in a film with a kinked crack at 80°C

The crack is then solicited by the sliding mode (Mode II). The stress intensity factor associated to this mode (K_{II}) was calculated (Fig.8).

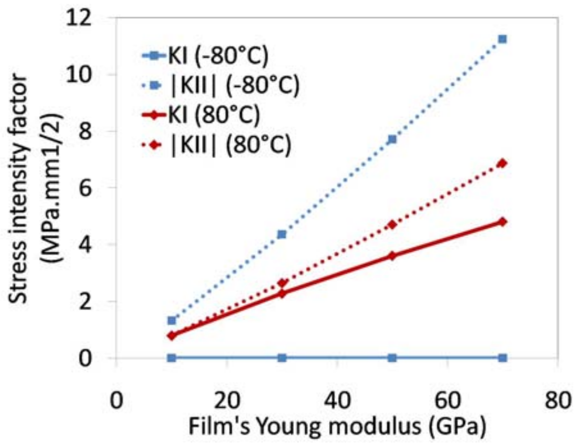

Fig.8. Evolution of K_I and K_{II} with the young modulus of the film at -80°C and 80°C for crack depth of 17 µm

At 80°C, the crack is solicited in a mixed mode (I and II) while there is a pure mode II at -80°C. The value of K_{II} is mainly depending on the temperature difference with the reference (20°C), thus K_{II} (-40°C) ≈ K_{II} (80°C). That explains that the value of K_{II} at -80°C is much higher than at 80°C.

Both hot and cold parts of thermal cycles are thus able to lead to crack propagation parallel to the interface.

Fig.9 shows that the maximum stress intensity (K_I and K_{II}) factor is obtained when the crack kink is the deeper in the film, whatever the considered temperature.

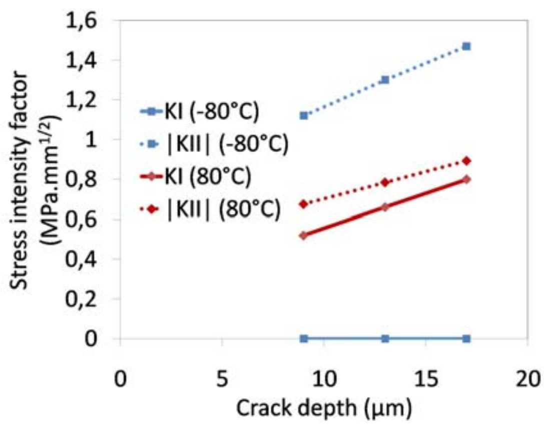

Fig.9. Evolution of the stress intensity factor in a film (E_f = 10 GPa) with the kink's crack depth.

Thus, defects (bubbles) near the interface are more likely to propagate under thermal stresses. Hot temperature (> 20°C) would lead to propagation under mixed mode while cold temperatures (< 20°C) are loading the crack with pure mode II. Crack propagation could lead to a decrease of the critical load measured by scratch-test or the failure of the peel-test. Fig.10 shows a cross section of a black anodic film (50%

porosity) after 10 cycles between -80°C and 80°C: the crack effectively grew near the interface.

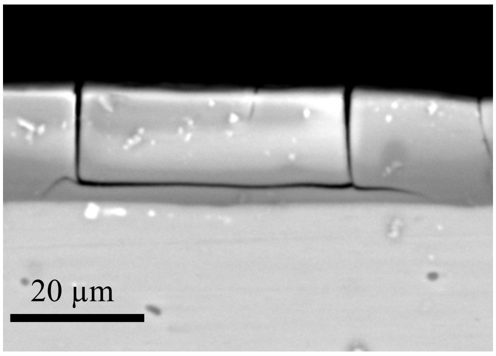

Fig.10. SEM observation of the cross section of a black anodic film after 10 cycles between -80°C and +80°C

4. CONCLUSION

Before any ageing, no adhesion anomaly is detected on black anodic films, in spite of the presence of cracks due to the process.
Adhesion of these films can be affected by thermal cycling. When it is the case, peel-test and scratch-test reveal the anomaly after the first cycle.

The anodizing temperature seems to be a key parameter for flaking problems. Actually, an increase of 5 degrees changes the initial porosity of the film from 40% to 50%. As a result, black films anodized at 20°C are not visibly affected by ageing between -80°C and 80°C while films realised at 25°C are flaking.

Numerical simulation has shown that hot temperatures can generate crack propagation through the thickness of the film in opening mode.
If the crack is deep enough, a defect in the film (oxygen bubbles for example) can initiate a cracking near the interface film/substrate. The propagation along the interface could then occur under pure mode II or under mixed mode. It would result in the detachment of particles and possibly in the pollution of particles.

Before ageing, cracks in films with 50% of initial porosity are wider and probably deeper than in the film with 40% of initial porosity. The small difference of young modulus between those two types of films is not explaining the difference of behaviour observed during ageing. The more porous films may have a lower critical stress intensity factor leading to easy crack propagation. Thus, thermal stresses between -80°C and +80°C may then be sufficient to cause propagation along the interface only in the films with the highest porosity, resulting in the decrease of adhesion observed.

5. AKNOWLEDGEMENT

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6. REFERENCES

1. Shrestha S., et al. Microstructural and thermo-optical properties of black Keronite PEO coating on aluminium alloy AA7075 for spacecraft materials applications, *Proceedings of ISMSE & ICPMSE, SP-616*, ESA Publication Division, Collioure, France, s1.5.1-9., 2006.

2. McCroskey D.M., et al. Aeroglaze Z306 black paint for cryogenic telescope use: outgassing and water vapor regain, *The International Society for Optical Engineering (Ed.) Proceeding SPIE*, 119-128, 2000.

3. Goueffon Y., et al. Black anodic coatings for space applications: Study of the process parameters, characteristics and mechanical properties, *J. Mater. Process. Tech.*, Vol. 209, 5145-5151, 2009.

4. Sharma A.K., et al. Anodizing and inorganic black coloring of aluminum alloys for space applications, *Met. Finish.*, Vol 95, 14–20, 1997.

5. LeVesque R., et al. Black anodize as a thermal control coating for space station freedom. *AIAA-92-2160-CP, In AAIA Technical papers (A92-31285 12-23)*, Washington, USA, 56-65, 1992.

6. Goueffon Y., et al. Chemical characteristics, mechanical and thermo-optical properties of black anodic films prepared on 7175 aluminium alloy for space applications, *Mat. Chem. Phys.*, in press.

7. ESA ECSS-Q-70-03A, Black anodizing of metals with inorganic dyes, 2006. http://www.ecss.nl.

8. Scherer A., et al. Optimization and microstructural analysis of cobalt-sulphide-pigmented aluminum oxide, *Thin Solid Film*, Vol. 101, 311-328, 1983.

9. Goueffon Y., et al. Mechanical behavior of black anodic films on 7175 aluminium alloy for space applications, *Surf. Coat. Tech.*, 2009. doi:10.1016/j.surfcoat.2009.06.026

10. Zhao X., et al., The cracking behaviours of anodic films on 1050 and 2024 aluminum alloys after heating up to 300°C, *J. Alloy Comp.*, 479, 2009, 473-479.

11. Liu W., Zuo Y., Chen S., Zhao X., Zhao J., The effects of sealing on cracking tendency of anodic films

on 2024 aluminum alloy after heating up to 300 °C, *Surf. Coat. Tech.*, 203, 9, 2009, 1244-1251.

12. Zhou J., et al. Research on the thermal expansion behavior of anodic films on aluminium, *Thin Solid Films*, Vol. 346, 280-283, 1999.

13. Goueffon Y., Etude et simulation des mécanismes de dégradation de revêtements anodiques noirs sur alliage d'aluminium pour applications en environnement spatial, *thèse de doctorat de l'université de Toulouse*, 2009.

14. Alwitt R.S., McClung R.C., Jacobs S., Anodized aluminium coatings for thermal control, Part I: Coating process and stresses, *AIAA-922158-CP, AIAA Technical Papers (A92-31285 12-23)*, Washington, USA, 1992, p. 39-45.

15. Wernick S., et al. *The Surface Treatment and Finishing of Aluminium and its Alloys*, Fifth Edition, Vol. 2, , Teddington-England, Finishing Pub. LTD & ASM Intert. Ed. 1987.