

# Advanced plasma electrolytic oxidation treatment for protection of light weight materials and structures in a space environment

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## INTRODUCTION

Light weight materials such as aluminium alloys are extensively used in spacecraft components. Protection of these materials in a space environment presents enormous challenge due to stringent requirements e.g. resistance to corrosion prior to launch, wear, cold welding and fretting impacts, stability in vacuum, resistance to severe thermal shocks, UV degradation, debris formation or outgassing. Other requirements include stable thermo-optical and high dielectric characteristics.

Equipment on-board the manned habitats of the International Space Station (Fig.1) can experience humidity levels up to 70% RH and also that spacecraft and equipment often have to be stored on earth for considerable periods of time and that during storage / launch and return to earth they are often exposed to corrosive environments. Also, the repetitive mechanical contacting of aluminium alloys in vacuum can lead to seizure by cold welding.



Fig.1 International Space Station (ISS). Courtesy of European Space Agency

Poor corrosion, wear and other functional characteristics of high strength aluminium alloys are well known, and as such, these alloys are always used with protective surface coatings which include chromating, metal spraying, paints, anodising.

Conventional black-anodised coatings with organic dyes used as spacecraft thermal control materials are considered not to have stable thermo-optical properties after environmental exposures in a space environment.

The recommended black anodising uses Nickel sulphide or Cobalt sulphide as an inorganic black dye [1]. These chemicals are considered to have environmental and health concerns. Even conventional hard anodising techniques are not fully environmentally friendly because of the use of strong acids and their disposal issues. Moreover, there is a limitation with the hard anodising process in achieving black finishes on certain aluminium alloys. Thus, there exists a strong need to identify new coating processes that can meet the requirements of recent environmental legislation and a continual drive for better coating performance.

## PLASMA ELECTROLYTIC OXIDATION

Plasma electrolytic oxidation is one of relatively new environmentally safe electrolytic coating processes, applicable to light metals and their alloys and represents a rapidly developing sector in surface engineering. The process involves the use of higher voltages than in anodising and the electrolyte usually consists of low concentration alkaline solutions and all variants of this process are considered to be environmentally friendly. The process results in the formation of a ceramic layer that offers protection to the base alloy in terms of corrosion, wear and offers other functional characteristics including thermo-optical, dielectric, thermal barrier, low friction coefficient and also can be used as pre-treatment for topcoat paints and other metal/ceramics to create composite coatings. A number of processes are being offered by research laboratories and commercial companies around the world. These available processes differ in terms of coating deposition rate and thickness limit, applied voltage, electrolyte type, electrolyte life, phase formation, process speed and scalability etc. The process has demonstrated significant interest in offering improved surface treatment to Mg and Al alloys and as a replacement for conventional acid based processes such as DOW and other chemical processes that contain hexavalent chrome, and including anodising processes.

**Table 1** Typical process parameters during Keronite PEO and hard anodising of AA7075 alloy

Coating process	Aluminium alloy	Pre-treatment	Electrolyte	Total salt content (%)	Typical pH	Nominal thickness (µm)	Coating rate (µm/min)	Voltage (V)	Process temp (°C)	Coating formation method	Surface appearance
Keronite (AC)	7075	Degrease only	Proprietary alkaline free of Cr, V or other heavy metals	< 4	7-12	15-60	1 - 4	200 - 900	12 to 30	Plasma oxidation	Grey to Charcoal black
Hard Anodising (DC)	7075	Degrease and chemical clean in alkaline solution	Sulphuric acid H <sub>2</sub> SO <sub>4</sub>	10 - 20	<3	< 60	0.8 - 1	45 - 50	-10 to 0	Oxidation without plasma	Bluish Black

The Keronite<sup>®</sup> is an advanced surface technology based on plasma electrolytic oxidation. It is an environmentally friendly and safe process for the preparation of corrosion and wear resistant black finish [2] ceramic layers on aluminium alloys that has seen increasing interest over recent years in aerospace, defence, optical instruments and general industrial applications. The Keronite process employs a low concentration alkaline / neutral solution that is free of heavy metals with salt concentration < 4%. Unlike Keronite, most commonly used sulphuric acid hard anodising uses 10-20 vol. % of acid concentration. Some parameters for the Keronite PEO and sulphuric acid hard anodising processes are given in Table 1.

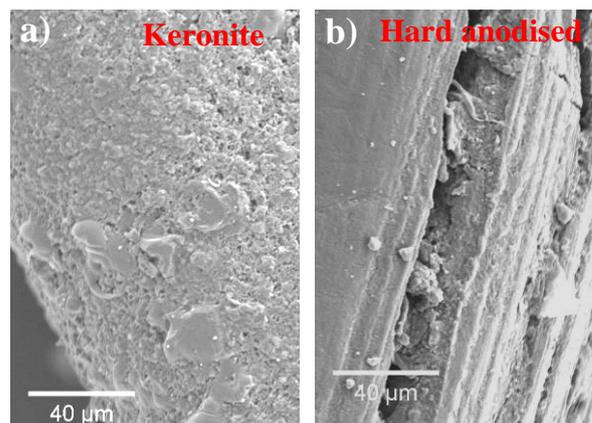


*Fig.2 Plasma discharge around a component immersed in electrolyte*

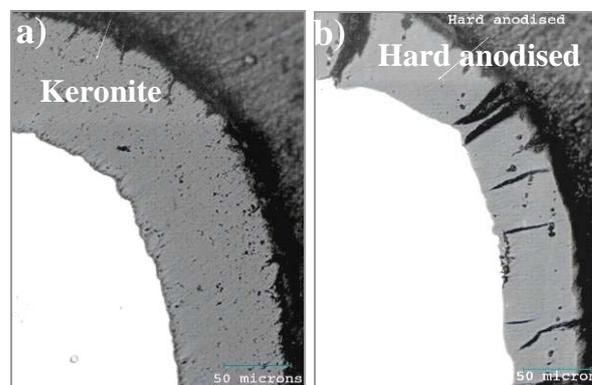
Coating of aluminium alloys using the Keronite plasma electrolytic oxidation (PEO) process involves creation of a plasma discharge around a component immersed in an electrolyte (Fig.2). The mechanism of oxide layer formation during the Keronite PEO process represents complex combinations of oxide growth with subsequent fusing, re-crystallisation of the oxide film and also involves partial substrate metal dissolution at microscopic levels. While the Keronite PEO process can be considered very aggressive due to extensive plasma discharges on the surface and oxide eruptions at very high local pressures (believed to be several GPa) but these discrete processes occur at microscopic levels and the treated component including the working surface receive no heat affected zones or distortion. The process temperature and the component are typically in the range of 12-30°C. The resulting oxidation of the alloy surface can also include some elemental co-deposition from the electrolyte, creating a ceramic layer that contains both crystalline and amorphous phases.

## COATING CHARACTERISTICS

An SEM image of an as-prepared surface of the Keronite layer is shown in Fig.3a which depicts an abundance of spherical and irregular shaped particles-like structures that were formed during the PEO process. An as-prepared surface of the hard-anodised layer is shown in Fig.3b which shows several voids and micro-porosity on the coating surface. In addition, the surface clearly shows parallel lines that form vertical through thickness cracks.



*Fig.3 SEM images showing a sharp edge/corner of the coating on AA7075: a) good and uniform coating retention with the Keronite layer; and b) wide-opening cracks with the hard anodised layer[3].*



*Fig.4 Optical micrographs of: a) Keronite coating showing a uniform coating coverage and good edge retention; and b) hard anodised coating showing extensive V-shaped through thickness columnar cracks extending down to the substrate on the edge.*

**Table 2** Characteristics of Keronite PEO coatings on aluminium alloys.

Coating type	Alloy	Colour	Roughness (Ra, $\mu\text{m}$ )	Porosity (%)	Phase composition	Hardness (HV)	Corrosion resistance (hrs)	Solar absorptance ( $\alpha_s$ )	Thermal emittance ( $\epsilon_n$ )	Reflectance (%)	UV resistance	Vacuum outgassing (TML%)	TSR -196 to +100°C
Keronite black Type 1	2219	Grey to charcoal black	1-1.6	<5	Crystalline alumina	1200-1550	> 360	0.88 - 0.89	0.71-0.75	-	Pass	-	Yes
Keronite black Type 1	7075	Grey to charcoal black	< 1	<2	Crystalline alumina	1600-1650	> 360	0.81-0.83	0.70-0.72	-	Pass	< 0.1	Yes
Keronite new black Type 2	6082	charcoal black	1-1.5	30-50	Amorphous alumina	500-1200	> 1000	0.94	0.84	0.1	Pass	-	Yes

<sup>1</sup> - ASTM B117; TSR - thermal shock resistance, UV resistance - grey scale rating  $\geq 4$ .

A typical cross section of the Keronite layer on AA7075 alloy at the outer corner / edge is shown in Fig.4a. The Keronite layer, although, has some micro-scale porosity as would be expected from the PEO process but the coating can be considered relatively dense. A typical cross section of the hard-anodised layer on AA7075 alloy at the outer corner is shown in Fig.4b which shows the presence of extensive 'V-shaped' columnar cracks. These cracks are seen through the entire coating thickness and extend down to the underlying substrate, and in several areas even expose the bare metal substrate. Some general characteristics of the Keronite coating on three different aluminium alloys are given in Table 2.

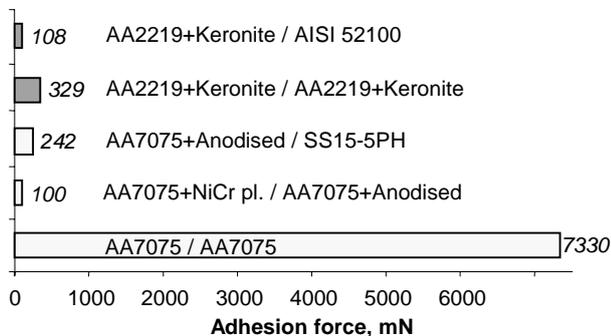


Fig.5. Adhesion measured during fretting tests [2].

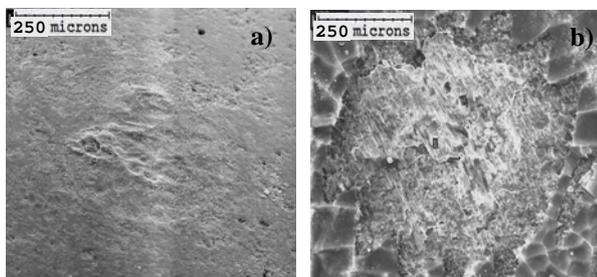


Fig.6. Surface after fretting test of: a) Keronite coating (no visible damage) and b) anodised coating (showing extensive surface cracks) [2]

The Keronite ceramic surface after fretting tests in vacuum was shown to have very low adhesion as shown in Fig.5 which shows that adhesion values of the Keronite coated AA2219 against a 52100 steel ball

and NiCr plated AA7075 against an anodised AA7075 are similar. An aluminium alloy without a coating resulted in extremely high adhesion after fretting. The Keronite coating surface against itself displayed a higher adhesion than against a steel surface by about three times. Despite low adhesion values displayed by the Keronite and hard anodised coatings against steel surfaces, the Keronite coating displayed superiority over the anodised coating. The Keronite coating shows no sign of surface damage, whereas, the anodised coating displayed extensive cracking and chipping of the coating surface in a fretting environment. The differences in the damage mechanisms between the Keronite and anodised coating surfaces are shown in Fig.6.

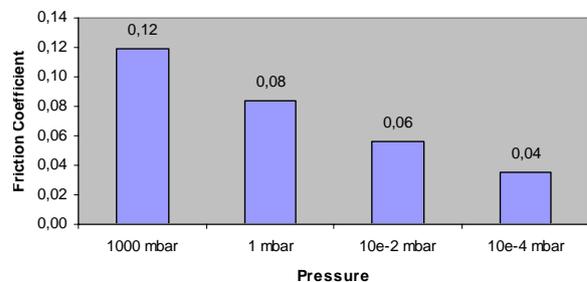


Fig. 7 Friction coefficient of Keronite + MoS<sub>2</sub> composite coating after extreme wear tests in a cryogenic environment. Courtesy: Instituto de Astrofísica de Canarias

While the friction coefficient of Keronite to Keronite has been reported relatively high about 0.5-0.6 [2], this can be substantially reduced to an extremely low value of about 0.04 by impregnating the porosity in the coating with solid lubricants e.g. MoS<sub>2</sub> (Fig.7). Recently, Instituto de Astrofísica de Canarias (IAC) and Keronite have undertaken a co-operative research on cryogenic plain sliding bearings. Keronite + MoS<sub>2</sub> composite coating has been developed as a tribological surface with a low sliding friction coefficient, maximum resistance to wear, minimum debris generation, vacuum compatibility, resistance to thermal shock and thermal conductivity better than plastics.

Keronite PEO coatings on Cu containing aluminium alloys such as 2219 and 7075 can be prepared black and these have been extensively studied by the European Space Agency as thermal control coatings. Recently there has been growing interest by industries on black finish coatings on other aluminium alloys. In this regard, Keronite International Ltd. has recently developed an industrial scale PEO process capable of producing a charcoal black finish on most wrought and some cast aluminium alloys. Unlike the process discussed above, this new process converts the aluminium alloys into a black finish and the resulting surface characteristics and properties are not dependent on the substrate alloy composition [4]. A typical SEM image of this new black Keronite surface is shown in Fig.8.

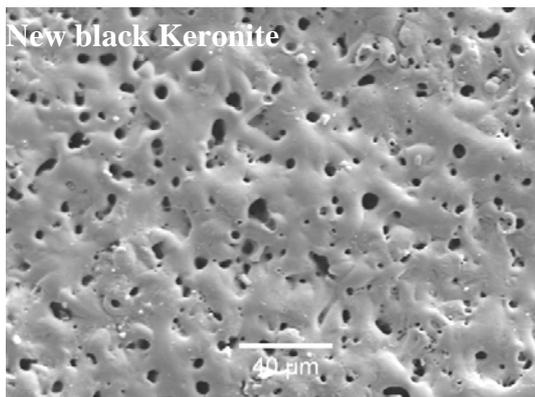


Fig. 8 SEM image of new black Keronite on AA6060 alloy showing coating surface morphology with crater-like porosity.

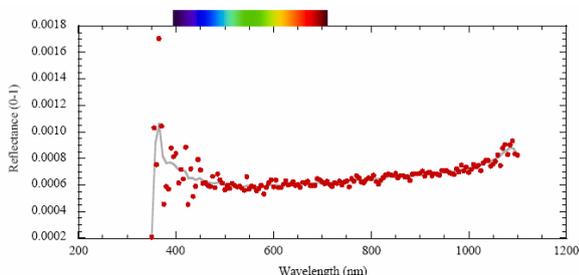


Fig. 9 Reflectance from the surface of a Keronite black sample, measured at 25°C with a fixed angle of incidence of 30 degrees [5].

This coating surface has very low reflectance of about <0.1% (Fig.9). This reflectance value is less than reported reflectance values for super black Ni-P coating and significantly less than that for black sulphuric acid anodised coating and black paints.

## APPLICATIONS

Keronite coatings have been extensively evaluated by ESA for spacecraft material applications as thermal control coatings. More studies have been made by Instituto de Astrofísica de Canarias, Spain for cryogenic bearing applications (Fig.10) and by Cilas Marseille for satellites (Fig.11) with extremely good results. Several other studies for various space and aerospace applications are currently underway on

Keronite coated parts including sun sensors (Fig.12-13).



Fig. 10 Keronite + MoS<sub>2</sub> composite coating on EMIR GRISM cryostat wheel bearing currently used for space observation. The coating has been extensively evaluated for wear resistance, debris formation, stick-slip behaviour, ultra-low friction. Courtesy: Instituto de Astrofísica de Canarias



Fig. 11 Barrel for satellites treated with new black Keronite. The black Keronite coating has recently been extensively tested in humidity, vibration, debris formation, low optical reflectivity tests and as a sub-layer for adhesive bonding. Courtesy: Cilas Marseille

CNES, ESA, the University of Southampton and ONERA have participated in a cooperative effort to develop a test-bed called the Material Exposure and Degradation Experiment (MEDET) to be launched in December 2007. Keronite coated thermal control micro-calorimeters are mounted on the MEDET flight hardware (Fig.14) that will be located on the external payload facility of ESA's Columbus Laboratory on the International Space Station.

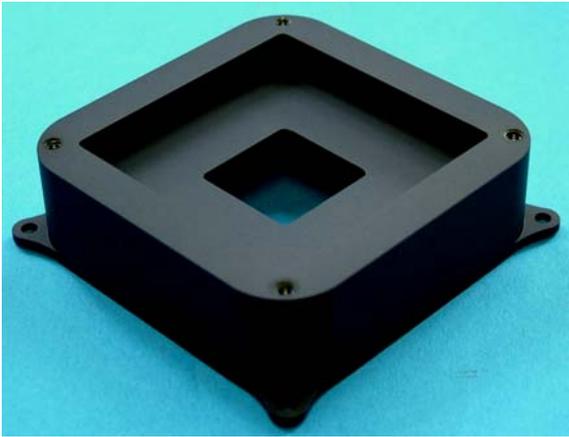


Fig. 12 Fine sun sensor (FSS) Baffle treated with black Keronite.

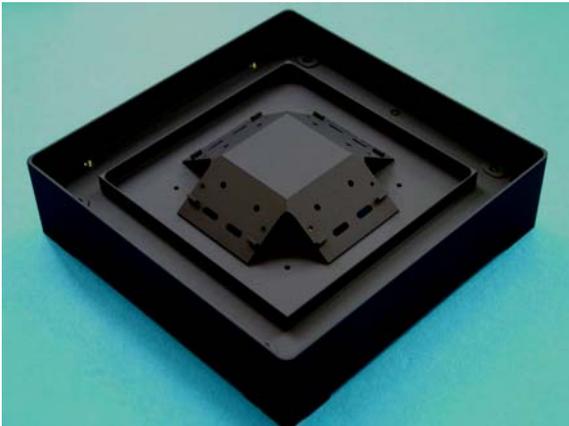


Fig. 13 Coarse sun sensor (CSS) Housing treated with black Keronite.



Keronite coated micro-calorimeter

Fig. 14 Keronite coated micro-calorimeter part mounted on the MEDET system for the International Space Station. Courtesy: MEDET Project.

## CLOSURE

Aluminium alloys represent attractive materials for spacecraft structures but they have been only selectively used to-date for mechanical parts, the key reasons for this, being the inherent problems with

corrosion and wear. In addition, the use of conventional paints and electrolytic surface modifications offer only limited surface enhancement.

Plasma electrolytic oxidation is an emerging surface technology and has received growing research and industrial interests in the last decade due to its environmentally friendliness and extremely good surface properties which are often unachievable by other coating routes [5-7]. While PEO has become an acceptable surface modification platform for light metal alloys, further industry support and research will be required to optimise the process to suit individual industry standards and requirements and make this novel surface modification process economically more viable and globally acceptable.

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