Reactivity of Al alloys during and after surface treatment (PhD CIFRE)

PhD director: Professor Kevin Ogle, Chimie-Paristech, PSL University
Laboratoire d'accueil : Institut de Recherche Chimie Paris, IRCP

Financement: CIFRE. Employer: Institut de la Corrsion, Brest
Preferred starting date: Fall, 2019, negotiable.

The goal will be to identify the mechanisms associated with the surface treatment of Al alloys and their ultimate degradation when exposed to humid atmospheres using state of the art, *in situ* spectroscopic and electrochemical techniques.

As a CIFRE recipient, you will be employed full time by the *Institut de la Corrosion*, Brest, France. IC is part of the RISE group (Sweden) with about 2700 employees in France and Stockholm, one of the world's largest private research and consultancy companies specialized in corrosion. The project will require national and international mobility between the *Ecole Nationale Supérieure de Chimie de Paris* (ENSCP, Paris France), the *Institute of Corrosion* in Brest, France and *RISE* in Stockholm, Sweden. A possible distribution of time: 18 months in Paris, 12 months in Stockholm, 6 months in Brest.

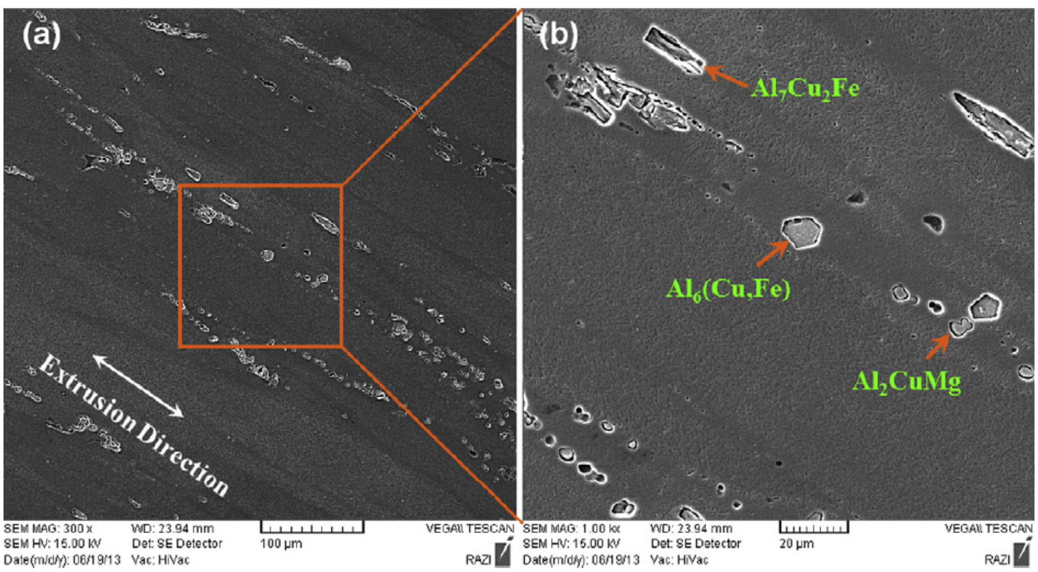
Profile:
(1) A Masters degree or equivalent in chemistry or related field, preferably with a strong background in materials, electrochemistry and/or corrosion,
(2) Good hands-on laboratory skills,
(3) Mobility, and a desire to work in an international environment,
(4) A good level of English.

To apply, send a curriculum vitae and letter of motivation with references to
Professor Kevin Ogle (ENSCP, Paris), kevin.ogle@chimieparistech.psl.eu
preferably before 31 May.

Other contacts:
Dr. Dominique Thierry (IC, Brest): dominique.thierry@institut-corrosion.fr
Dr. Dan Persson (RISE, Stockholm): dan.persson@ri.se

Summary of Project

Context Aluminum is one of the most common elements in the earth's crust with a very low density, good mechanical properties, and is remarkably easy to recycle. In its pure state, aluminum metal is intrinsically resistant to corrosion forming a passive film of Al oxides of only a few nanometers thickness. However, it is often necessary to add additional alloying elements to enhance its mechanical properties through a metallurgical process known as precipitation hardening. The surface of the final alloy is a complex heterogeneous system consisting of a nearly pure Al matrix speckled with precipitates of various intermetallic particles enriched in the alloying elements such as Cu, Mg, Fe, Zn, and Si. These particles lead to a significant deterioration in the corrosion resistance as compared to pure aluminum. The intermetallic particles on the surface of a common alloy, AA 7075, used in the aerospace industry, is shown in the SEM photo below.



Microstructure of AA7075.

To reduce the effect of the intermetallic particles, the materials undergo a chemical surface treatment which either removes them or passivates them such that the overall electrochemical activity of the surface becomes uniform. Different processes are used in different industries but a typical process might include the following:

1) Etching: A significant thickness of the Al alloys is removed by dissolution in either strong acid or base.
2) Deoxidation: Residual oxides and particles of metallic Cu are removed, frequently with HNO_3 which also passivates the Al.
3) Conversion coating (or anodization) which deposits a new oxide film on the surface
4) Application of a polymer film.

Overview of the Project:
This project is divided into three work packages that will be performed in Paris, Brest, and Stockholm respectively.

1. The fate of the elements during surface treatment (Paris).
The goal will be to identify how the different particles and elements interact with the sequence of chemical treatments to form the final AA/oxide product during the first three surface treatment steps. This will be based on the *in situ* measurement of the elemental dissolution rates of the alloy during the etching, deoxidation and conversion, using a novel, state of the art technique, atomic emission spectroelectrochemistry (AESEC). The specific formulations and alloy compositions will be decided after a preliminary bibliographic study. To further clarify the interactions between phases, the reactions of with synthetic pure intermetallics will be investigated, such as Al_2Cu, Al_2CuMg, Al_7Cu_2Fe, Zn_2Mg $MgSi_2$. This methodology coupled with *ex situ* microscopic and surface analytic characterization of the material should permit a detailed analytical description of the reactions occurring between material and electrolyte during each step of the process, and to clarify the fate of each element and phase and qualify their interactions with each other.

2. Corrosion mechanisms at the buried alloy/oxide/polymer interface (Brest).
The goal will be to understand how the surface treatment process affects the mechanisms of corrosion after application of a polymer film following surface. For this situation, the corrosion activity is buried underneath the polymer film and specialized electrochemical instrumentation is required to observe its evolution. The spatial distribution of the electrochemical activity may be visualized using a technique known as the scanning Kelvin probe. In this way, we can identify regions of anodic and cathodic activity and directly observe *in situ* the rate at which they move around underneath the polymer coating or at artificial defects. Measurements will be performed both on pure phases and aluminum alloys. This activity will then be related to the nature of the surface as obtained from the result of Objective 1. This part of the activity will be performed at the facilities *of Institut de la Corrosion* in Brest.

3. Bonding and adhesion at the alloy/oxide/polymer interface (Sweden).
A third objective will be to further characterize the precise bond breaking mechanisms of the substrate / polymer interface that occur during corrosion at the oxide polymer interface. This will use *in situ* vibrational spectroscopy- attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and ATR- FTIR focal plane array imaging (ATR-FTIR FPA imaging), RISE, Sweden, to probe destabilization of the substrate / polymer interface and chemical transformations of the interfacial oxide when the system is exposed to electrolyte solution. The *in situ* spectroscopic measurement will be combined with simultaneous electrochemical impedance spectroscopy (EIS) measurements which will provide complementary information about the corrosion processes at the interface. This part of the activity will be performed at the facilities of *RISE* in Stockholm.