

The role of alloying elements on the dissolution, passivation, & corrosion of high entropy alloys

Supervisor :

Professor Kevin Ogle, Chimie-ParisTech
kevin.ogle@chimieparistech.psl.eu



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11, rue Pierre et Marie Curie, Paris 05

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DESCRIPTION

The project is supported financially by the *Agence Nationale de Recherche* (ANR, Project Tapas2020)

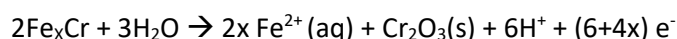
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High entropy alloys (or multi-principal element alloys) represent an emerging class of materials consisting of five or more alloying elements in nearly equimolar concentrations. These alloys have demonstrated an exceptional combination of properties such as high strength and ductility, improved fatigue resistance, fracture toughness, and thermal stability and show considerable potential for use as corrosion resistant materials especially in extreme environments. The absence of a single primary element in the HEA, however, makes alloy development extremely difficult. This is especially true as concerns the optimization of corrosion resistance which depends on the chemical and electrochemical interactions of the individual alloy elements.

The goal of this project is to identify the role of the individual alloy elements on the mechanisms of passive film formation and corrosion. These results should open a path towards the identification of the optimum composition / microstructure for corrosion resistance by offering a science-based guide to navigating the complex alloy compositional space.

Background

The corrosion resistance mechanism associated with these alloys is similar to that of many other alloys such as the Fe-Cr family (stainless steel). It involves the formation of a nanometric oxide film at the surface of the alloy which protects the metallic substrate from the environment. For a simple Fe-Cr binary alloy in an acid solution, the main oxidation process may be thought of as a selective dissolution of Fe:



The reaction stops as soon as the $\text{Cr}_2\text{O}_3(\text{s})$ film is formed protecting the underlying metal from corrosion. The situation for a high entropy alloy however is far more intricate. One of the more common HEAs, the Cantor alloy, consists of Ni, Fe, Cr, Mn, and Co in equimolar composition. In this case, we expect considerable interactions between the alloying elements and the formation of mixed oxides which can hardly be predicted from first principles.

Questions to be addressed in this project include: What are the fates of the different alloying elements during corrosion and passivation? Do they dissolve into solution or incorporate into the oxide film? If in the film, how do they affect the barrier properties of the film? How are these phenomena and properties related to alloy composition and microstructure?

Experimental Aspects

The student will gain experience with a variety of electrochemical and *in situ* spectroscopic techniques as well as metallurgical elaboration and characterization.

Electrochemistry. Conventional electrochemical methods frequently used in this type of research are difficult to interpret for the HEA because of the large number of elements that may contribute to the electrochemical response of the alloy. This project will rely on a novel technique of element resolved electrochemistry to characterize the contribution of each individual alloying element to the dissolution and passive film formation of the alloys. The element resolved electrochemistry, or atomic emission spectroelectrochemistry, is a specialized technique that involves the coupling of a conventional electrochemical flow cell to an inductively coupled plasma atomic emission spectrometer. A review of the AESEC technique and its applications (Ogle, 2019), an example of its application to a high entropy alloy (Li, 2020) are available online.

K. Ogle, "Atomic Emission Spectroelectrochemistry: Real-Time Rate Measurements of Dissolution, Corrosion, and Passivation" *Corrosion Journal*, 2019(75)1398. <https://meridian.allenpress.com/corrosion/article-pdf/75/12/1398/2656216/3336.pdf>

Xuejie Li et al "Dissolution and Passivation of a Ni-Cr-Fe-Ru-Mo-W High Entropy Alloy by Elementally Resolved Electrochemistry" *J. Electrochem. Soc.* 167(2020) 061505. (<https://iopscience.iop.org/article/10.1149/1945-7111/ab7f86/pdf>).

Other electrochemical / spectroscopic methods:

Other techniques will be used as needed including conventional electrochemical techniques and in particular, electrochemical impedance spectroscopy (EIS), and various forms of surface spectroscopy such as X-ray photoelectron spectroscopy (XPS), glow discharge optical emission spectroscopy, etc.

Metallurgy: The synthesis and characterization of a high entropy alloys with variable composition and microstructure will be undertaken using specialized metallurgical processing methods. Microstructural characterization will be carried out with scanning electron microscopy, transmission electron microscopy, electron backscattered diffraction, and energy dispersive X-ray microanalysis.

Model film realization: The stability of the oxide film with variable environment and electrochemical conditions will be investigated by preparing model oxide films on inert substrates using radio frequency sputtering under vacuum. In this way the contribution of the passive film to the overall dissolution / corrosion mechanism may be distinguished from that of the substrate. This research will be conducted during short trips to the University of Brest.

Candidate Profile: The candidate should have an Engineering and / or Master of Science degree with a good level of general and scientific culture and solid laboratory experience. Previous experience in one or more of electrochemistry, metallurgy, or applied spectroscopy would be an important asset.

The ideal candidate will be highly motivated for multidisciplinary research in an important, dynamic field. The candidate should possess good analytical, synthesis, innovation and communication skills with qualities of adaptability and creativity.

Excellent English skills are necessary. Our research group functions primarily in English, all publications will be in English, and participation in international conferences and visits to foreign laboratories will be expected.