Understanding Corrosion in 4D

An ONR funded Multidisciplinary University Research Initiative
The critical importance of corrosion, particularly rust has been known for centuries as have ways to mitigate it; for instance the 4th Century Iron Pillar in Delhi (above) is protected by a thin layer of misawite due to a high level of phosphorus in the cast iron. However, much of our current knowledge is from the mesoscale down to several nanometers. Multiple processes occur over wide spatial and temporal scales control the nucleation, stability, and utility of oxide scales. Creating quantitative models to disentangle the critical processes is highly prohibitive because of the time and costs of traditional experimental oxidation and corrosion studies.
As recognized in the 2011 report Research Opportunities in Corrosion Science and Engineering by the National Research Council, in the last decade there has been a convergence of forces creating the opportunity to reinvent our understanding of corrosion at the nanoscale. There has been an explosion of tools to image materials at the atomic scale and accurately calculate their behavior. Not only can single atoms be imaged, their chemical state can be measured. Modern ab-initio methods such as density functional theory are now starting to be able to handle materials such as transition metal oxides, where older functionals can go catastrophically wrong. Our intent is to bring the full power of these new tools to bear on corrosion at the atomic scale.

Right: TEAM 1.0 Electron microscope. ncem.lbl.gov
Towards A New Paradigm

The target of this five year program funded by the Office of Naval Research is to understand in detail the early-stage oxidation and aqueous corrosion in three selected model systems. We believe that a comprehensive experimental and theoretical attack will enable us to understand what matters, what does not, and lay the basis for a paradigm shift in improvements of corrosion-resistant materials. Our specific targets are:

- **NiCrAl alloys**, a classic two-phase high-temperature alloy with alumina or chromia protection.
- **MoSiB alloys**, a new class of alloys for higher-temperature applications with a self-forming glass protective coating
- **Aqueous corrosion resistant materials** with dopants effecting oxide growth that are used for many current marine applications.

Multiscale analysis of a corroded Co-Cr-Mo alloy
The problem requires a broad attack and unique methods and instrumentation. The team led by Marks builds on previous collaborations and aims to extend these to this multi-scale challenge. Our expertise include: Miao, UCLA (atomic resolution 3D electron tomography; coherent X-ray imaging); Marks, NU (TEM, surface science and oxide surfaces); Voorhees, NU (phase field simulations, 4D X-ray tomography); Perepezko, UWM (alloy design and modeling; multiphase microstructures and reaction kinetics); Heinz, UA (MD and Monte Carlo simulations of metal and oxide interfaces); Rondinelli, NU (electronic structure theory of oxides, DFT calculations; materials design), Reinke and Scully, UVA (aqueous corrosion, electrochemistry, scanning probe and spectroscopy).
And Beyond

Corrosion is not limited to military applications:

- Metallic biomedical implants can corrode in the human body leading to severe problems

- Oil and other pipelines can fail due to corrosion

Above: Hip implant, source www.zimmer.com

Left: corroded pipe, source www.daviddarling.info

We believe the same methods can be applied to a wide range of other corrosion related problems.
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