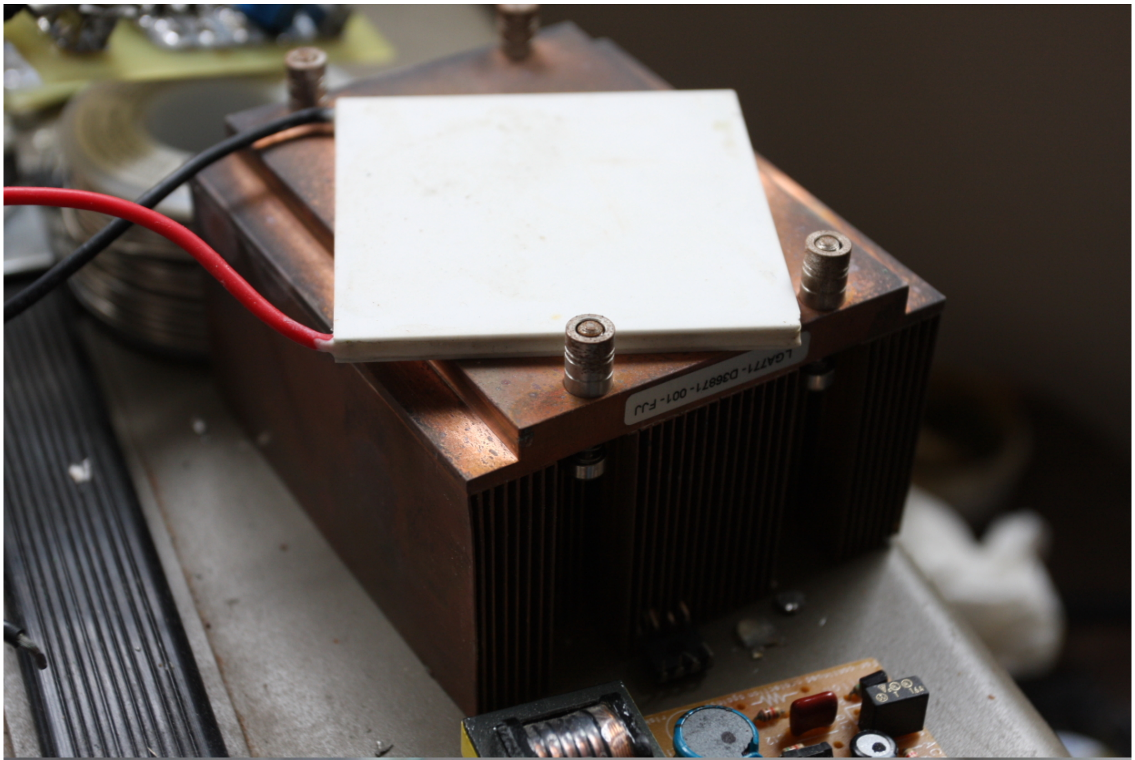
A Rusting Problem: Rust Everywhere!

By Danielle Costantino



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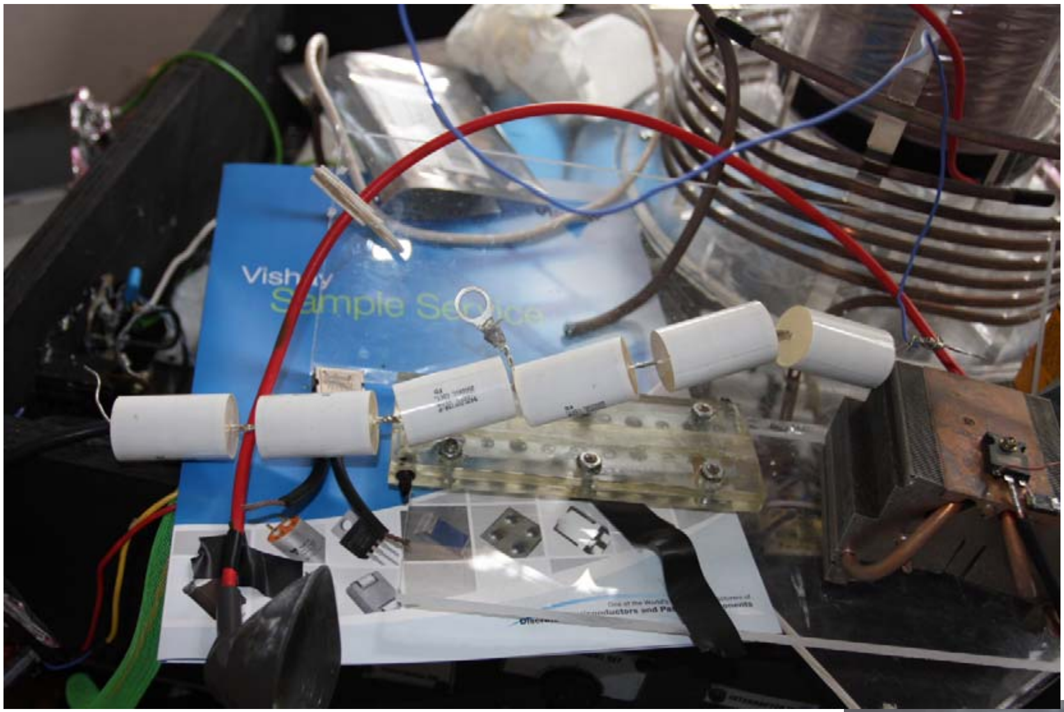
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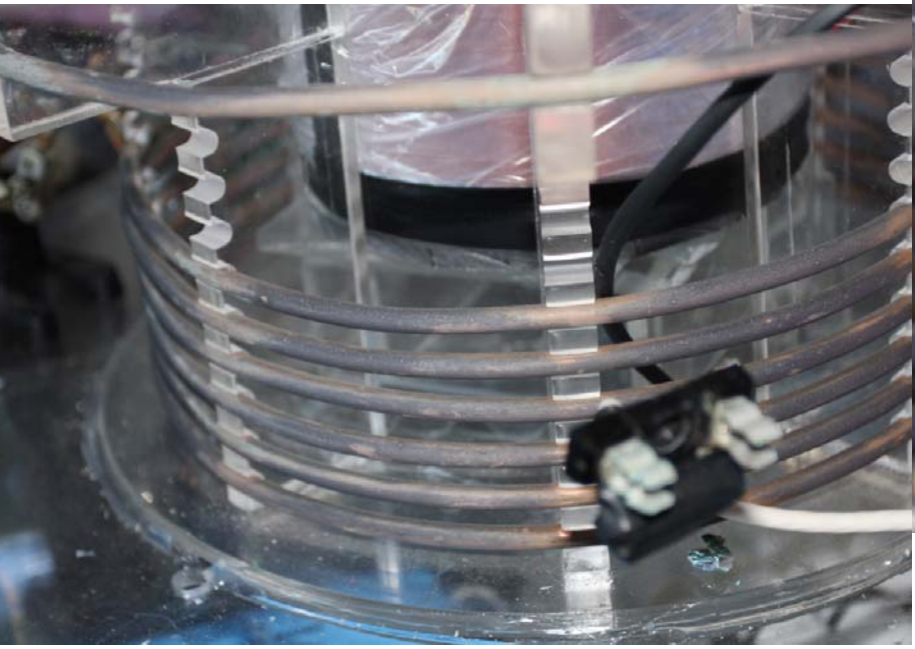
Sample Service

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Rust Everywhere

Possible Trigger Event:

- Flyback AC setup was run for about 10 min intermittent (runs were around 1-3 min) arcs estimated to be 6cm long (~60KV)* **

- Dc HV arcs were set at 20KV 2cm discharge from 0.025uF Cap bank, possibly 100 discharges**

*For part of tests, an arc lamp (Mg) was connected to the HV out
**(These tests were not conducted with the goal of rusting the metal in the room, or to produce Ozone)

<u>Background Information</u>

Corrosion Background:

Classification of spontaneous corrosion reactions

1) Film-free Chemical Interaction
    a) **Meta/Gas**
        i) Oxide or compound volatile (e.g. reaction of molybdenum with oxygen, reaction of iron or aluminum with chlorine).
    b) **Metal/Liquid**
        i) Reactions of solid metals with liquid metals (e.g. dissolution of aluminum in mercury)
        ii) Dissolution of metal in their fused halides (e.g. lead in lead chloride).
        iii) Dissolution of metals in non-aqueous solutions (e.g. reaction of aluminum with carbon tetrachloride).
2) Electrochemical
    a) Inseparable anode/cathode type (insep. A/C)
        i) Reactions with aqueous solutions. Uniform dissolution or corrosion of metals in acid, alkaline or neutral solutions (e.& dissolution of zinc in hydrochloric acid or in caustic soda solution.
        ii) General corrosion of zinc in water or during atmospheric exposure).
        iii) Reactions with non-aqueous solution (e.g. dissolution of copper in a solution of ammonium acetate and bromine in alcohol).
        iv) Reactions with fused salts.
    b) Separable anode/cathode type (sep. A/C)
        i) All reactions of metals in aqueous or non-aqueous solutions or in fused salts where one area of the metal surface is predominantly anodic and the other is predominantly cathodic so that the sites are physically identifiable.
3) Interfacial anode/cathode type in which the metal surface is filmed
    a) Metal/gas and metal/vapor reactions
        i) All reactions in which charge is transported through a film of reaction product on the metal surface-the film may or may not be rate determining (e.g. parabolic, logarithmic, asymptotic, etc. or linear growth laws, respectively).
    b) Metal/solution reactions
        i) All reactions involving the uniform formation and growth of a film of reaction product (e.g. reaction of metals with high-temperature water, reaction of copper with sulfur dissolved in carbon disulphide).

Source: CORROSION Volume I Metal/Environment Reactions, Edited by L.L. Shreir, R.A. Jarman, G.T. Burstein

Micro-arc oxidation (MAO):

Or spark discharge anodizing. Is a prosses in which an oxide layer is formed on a metal via plasma discharge anodization. It involves the modification of a conventional anodically grown oxide film by the application of an electric field greater than the dielectric breakdown field for the oxide. Discharges occur, and the resulting plasma-chemical reactions contribute to the growth of the coating.

The process may be applied to any valve metal such as aluminium, magnesium or titanium, and to a wide range of their alloys. Coating properties depend on the substrate alloy, but also on the electrolyte used and on the many parameters of the electrical system. On aluminum, dense alumina coatings (approximately 3% porosity) up to 130 microns thick can be formed, but more porous coatings up to 600 microns in thickness can also be formed by using different electrolytes. Typical alumina coatings consist of a relatively dense polycrystalline layer of alpha-alumina, with a softer, more porous layer of gamma-alumina formed on top.

(http://www.msm.cam.ac.uk/mmc/index.php/research/plasma-electrolytic-oxide-coatings)

Ozone:

O_3 (Ozone) is a strong oxidizer, unstable at high concentrations. Ozone decays to form O_2 (diatomic oxygen) in atmospheric conditions

$2\ O_3 \rightarrow 3\ O_2$

Ii is commonly produced using high voltage AC arc discharges:

$3\ O_2 \xrightarrow{\textit{electricity}} 2\ O_3$

Ozone will oxidize most metals (except gold, platinum, and iridium) to their highest oxidation state.

EX: $2\ Cu^+ (aq) + 2\ H_3O^+ (aq) + O_3 (g) \rightarrow 2\ Cu^{2+} (aq) + 3\ H_2O (l) + O_2 (g)$

Corrosion of Iron:

1) Reaction of iron with oxygen at room temperature or with oxygen or water at high temperatures - interfacial A/C type.
2) Reaction of iron with oxygenated water or with reducing acids inseparable - A/C type.
3) Reaction of iron containing a discontinuous magnetite scale with oxygenated water, crevice corrosion, water-line attack, ‘long-line’ corrosion of buried iron pipes, etc. - separable A/C type.

Source: CORROSION Volume I Metal/Environment Reactions, Edited by L.L. Shreir, R.A. Jarman, G.T. Burstein

Observations

Known Oxidized Metals	Known Metal Oxides Observed	Notes
Steel and Stainless Steel		Visible oxide passivation layer on stainless steel
Iron	Iron(III) oxide (Fe_2O_3)	Fe_2O_3 was seen covering all iron and steel
Cupper	Copper(II) oxide (CuO); Copper(I) oxide (Cu_2O)	CuO is present in greater quantities than Cu_2O at close proximity to ozone source
Aluminum	Aluminum oxide (Al_2O_3)	

Documented image gallery:

- http://img257.imageshack.us/gal.php?g=rust01.jpg
- http://img524.imageshack.us/gal.php?g=rust108.jpg

During and after tests:

- Strong pungent smell of ozone present, the test was stopped due to high amounts in air.

- No windows or doors were opened.

- No observable changes to metals at the time.

1 week after tests:

- Everything made of uncoated steel, iron, copper, brass, raw aluminum, and stainless steel were thourorly rusted.

- White/clear crystals observed to be deposited near and around setup.

- Steel wool flakes from polishing that were present in room became rust.

- Tools exposed to air were rusted, anything covered in any manner, partially or fully was either not rusted or very small traces of rust.

- Rusting occurred on everything metal that was exposed to the air in the test room, the larger room neighboring it (to a very high degree), and some doors and hinges in a hallway leading out, but rusting appears to diminish from the main and large room.

- Heavier rusting occurred on metal facing windows (exposed to sunlight)

- Air in rooms can be damp at times due to near by clothes dryer

***Possibly unrelated 1 week observations:**

- White/clear crystals observed to be deposited near and around setup. (contain Na) (salt from flame test)

- Etchant tank that was open to the air appears to have mostly evaporated (probably due to heat from sun) etchant is concentrated HCl (still present) H_2O and $CuCl_2$ (still present in high quantities) This was in the same room as the flyback.

Analysis

Because of ozone's properties of being a highly reactive oxidizer, it is the first obvious culprit for the rusting of the metals in the room. Although the amounts of ozone produced were high, higher levels have been present in the room for extended periods far longer than what was seen with the flyback run. This leads to the theory that another posses may have been involved in the oxidation of the metals. Another point leading to an unknown cause or effect is the wide range of metals effected. Under normal conditions stainless steel and aluminum are not easily oxidized to the extent seen on some near by pieces of metal by Ozone alone. These could have been caused by HCl gases evaporating from the open etchant containers. Another aid in the corrosion was noticed because of a difference in rust density on Cu tubing facing the sun vs the Cu away from the sun. One other factor contributing to the corrosion was the observed slight moisture in the air caused by a household dryer exhausting water vapor into the surrounding rooms. A leading factor could also be due to the AC plasma arc initiating a Micro-arc oxidation posses leading to the near by oxidation of aluminum and stainless steel.

Conclusion

All factors mentioned above could have contributed to the extensive rusting of the metals in the room but because these factors were present at comparable levels in prior instances the exact cause of the corrosion is still unknown. The only hypothesis for the extensive oxidation could be plasma MAO induced by the CW high voltage and high current AC electric arc discharge, sputtering plasma through the air and onto near by metals. The corona effect of this type of discharge could also have lead to the MAO of the oxide resistant metals.

Questions

What could have aided the ozone in causing the extent of oxidation seen on most uncoated metals in the room?