

Revisiting Some Vital Issues In Metallic Corrosion
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A number of important issues in corrosion should be re-visited. In this presentation we shall look at two.

1. Chromium

It was recently reported that it is considered that containers for storing radiating nuclear wastes for thousands of years will be constructed of a chromium-bearing alloy. Chromium is the major element in many corrosion resistant alloys. Additionally, chromate has been the basis of the most efficient chemical surface treatment of metals, and it were not for the toxicity of Cr^{6+} , this use would have probably continued indefinitely. All the newer “friendly” alternative, chromate-free, treatments are compared to the good old chromate recipes and some are even proclaimed to be almost as good. In all the practical cases in which chromium is used as a means of protection against corrosion- the reliance is on a thin and flimsy film, between 0.2 and 2 nm thick of the brittle trivalent oxide- Cr_2O_3 . Most users of chromium-based protection are either unaware, or oblivious, of the fact that the trivalent is the only chromium oxide out of the three of this element that is insoluble in water. This property alone is responsible for the extensive use of the element in corrosion protection. Both the divalent chromous oxide, and the hexavalent chromate oxides are water-soluble. Considering that Cr_2O_3 is stable at e.g. pH5 over only a narrow range of about 500 mV at 25C- must be alarming to the materials engineer. Additionally, the conversion of the trivalent oxide to halides renders it soluble. This is causing the high susceptibility of chromium-bearing alloys to crevice corrosion, and indeed to the propagation of pits. The “trans-passivation” to soluble chromates is not only causing corrosion problems at oxidizing conditions such as the special case of intergranular corrosion of stainless steel containers in re-processing of used uranium fuel elements in boiling nitric acid, but is also the root cause for the intergranular stress-corrosion-cracking of stainless steel fuel clad in high pressure water cooled nuclear reactors. Considering the unknown geological conditions that may prevail underground in thousands of years like temperature fluctuations, and changing oxidizing and reducing environments- the degree of confidence in the Cr_2O_3 film should be open to discussion.

2. The propagation of corrosion in pits and other occluded cavities.

Frankenthal and Pickering, in their pioneering work, have proposed that the potential drop that develops inside a propagating pit is causing the corrosion potential to drop from the passive range into the active range, and thus promote the advance of the corrosion front into the metal (1,2). This hypothesis has recently triggered the study of the propagation of filiform corrosion. The hypothesis should be discussed, at least for steels, in view of the fact that no passivity, in the conventional sense, can be expected inside pits at any potential- due to the chemistry of the trapped anolyte.

References

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2. H.W. Pickering, Corros.Sci.,29, 325 (1989).