ISSUES IN LONG-TERM BEHAVIOR OF THE PASSIVATING OXIDE FILM ON C-22 ALLOY

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July 2001

What is the passive film?

- essentially chromium (III) oxide.

Is molybdenum good for the passive film?

- no – Mo exerts its beneficial effect on localized corrosion in small cavities that are already dissolving. In fact Mo is bad for the passive film, especially at higher pH values where it readily dissolves out as Mo(VI)

How thick does the passive film grow?

- if there is no passive film dissolution, best "1/t" extrapolations suggest the thickness could be 5 nm after 1 year, thickening to only 7 nm after 10,000 years.

- if there is passive film dissolution (and re-precipitation), thick films could develop. Suppose film development is limited by some solubility of chromium and this is 10^{-14} molar (0.0005 ppb). Even this low solubility would permit a steady corrosion rate of ca. 1 nm/year, i.e. a film 10 μm thick could build up in 10,000 years if this material is re-precipitated.

How could the mechanism of film growth change?

- long-term corrosion potentials in the presence of oxygen and contaminants will reach the borderline of transpassivity for this alloy, especially at pH values higher than neutral.

- transpassivity means the onset of oxidation of the passive film, possibly Cr to soluble Cr(VI); certainly Mo to Mo(VI)

- This is an alternative reason why the passive corrosion rate might level out instead of falling with 1/t.

Can a thicker film be bad?

- a thick deposited (nanoporous) corrosion product film may promote stability of pits so that they occur on the free surface under environmental conditions normally associated with corrosion in tight crevices. This might involve anion-selectivity of the corrosion product, holding the aggressive solution against the metal surface.

- this is not a problem if the temperature has fallen sufficiently or oxygen is in short supply (or the material is not immersed).

How does metallurgy affect the passive film?

- welds are less corrosion-resistant as they have spatial variations in Cr and Mo content.

- very large areas of metal are certain to have flaws such as large inclusions or fabrication defects.

- phase transformations depleting Mo and Cr locally may occur over long periods of time (depending on the temperature)