Anodic Kinetics of NiCrMo Alloys
During Localized Corrosion

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The artificial pit or pencil-electrode technique has been used to quantify the anodic kinetics of a series of NiCr[Mo] alloys during localized corrosion in NaCl solution.

Ni-22Cr-xMo alloys were prepared at Ames Laboratory, with x = 0, 3, 6, 9 and 13 (compositions in weight percent). They were drawn into 125 μm wires which were mounted in resin, exposing one end. By applying an anodic potential in 1M NaCl solution, uniformly dissolving corrosion cavities could be created. Temperatures from 70 to 90°C were used, and a few critical comparisons with type 316 stainless steel were made for continuity with earlier work.

After dissolving for some time in a diffusion-limited condition with an anodic $NiCl_2$ salt film on the surface, with a final anodic limiting current density of ca. 1 A/cm^2, the electrodes were subjected to various potential programs designed to extract the anodic kinetics over a full range of potentials and local chemistries, covering 3 or 4 (potentially 6) orders of magnitude in current density.

The simplest program was a rapid potential backscan through the open-circuit potential, allowing the salt film to dissolve but freezing the local chemistry close to the saturation condition for the whole duration of the scan. Suitable IR correction enabled the extraction of rational 'Tafel' lines for the anodic process in the cavity. These were mostly conventional in appearance, with three subtleties:

- all the alloys showed some perturbation of Tafel linearity near the limiting current;
- the 13Mo alloy had an abnormally high series resistance, possibly due to a porous insoluble solid in the cavity, but this conclusion awaits cross-sectional microscopy;
- the 3Mo alloy showed a distinct two-stage dissolution, with the full inhibiting effect of alloyed Mo only taking effect above a certain current density.

Comparison with type 316 stainless steel showed that the Ni base alloys had much lower anodic limiting current density for a given depth of cavity (i.e. lower product of solubility and diffusivity) and lower open-circuit potentials in the cavity at comparable Mo content. Information on the hydrogen evolution kinetics was also obtained.

A notable improvement on earlier work on stainless steel was the use of improved instrumentation, enabling the fast measurement of dissolution kinetics relevant to crevice corrosion in a 'pit' geometry.

Slow backscanning of the potential from the diffusion-controlled condition should allow the chemistry in the cavity to follow the current, maintaining a linear concentration gradient of dissolved cations in the cavity. In principle, this should give a sudden repassivation when the combination of chemistry, potential and alloy reaches a passivation condition. This was almost never observed in its pure form, because the system is unstable against perturbations in the interface geometry (for example, undercutting of the alloy surface) that protect the dissolving surface against dilution of the acid anolyte solution. However relatively steep declines in current density were observed at critical current densities or chemistries.

A key type of experiment was the use of potential steps from the diffusion-limited regime to values near the open-circuit potential for the cavity. This is the ultimate use of the pencil-electrode method to investigate kinetics similar to those occurring in deep and/or narrow crevices. Finite difference modeling was used to model the evolution of the interfacial chemistry with time after the potential step, and checked against the effect of cavity depth on the current transients resulting from such potential steps. This may allow the rationalization of effects due to concentration-dependent diffusivity and other phenomena peculiar to concentrated salt solutions. It was immediately apparent that the Ni base alloys repassivated with more difficulty than stainless steels at low potentials, other things being equal. A possible explanation is that Fe-based systems more easily enrich oxidized Cr on the surface, leading to passivation, whereas a NiCr-base system needs to be driven harder (i.e. reach a higher potential) to passivate. This is not a concern with alloys with very high Mo contents such as 13%, but it does suggest that Ni base alloys in general have a slightly reduced resistance to slow propagation of crevice corrosion, compared with stainless steels, Mo and other factors being equal.

It is possible that the laboratory-prepared, ternary alloys such as those used in this investigation lack minor elements that may be present in commercial alloys, such as Si or Cu (for example), so comparisons with stainless steels may require a more complete base alloy chemistry to be made with certainty. This could form the basis of a useful future investigation.

From the application point of view, a key observation was the apparent appearance of an additional inhibiting factor, possibly a porous solid, between 9% and 13% Mo. It is not immediately apparent that this corresponds to some percolation or gelation threshold, but considering that Mo is known to form polymeric complexes in acid aqueous solution, this is an interesting possibility.