Fundamental Reasons For The Good Performance Of Alloy 800 In Nuclear Steam Generators

Zoe L. Coull, Roger C. Newman, Anatolie G. Carcea and Dorota M. Artymowicz

University of Toronto, Department of Chemical Engineering and Applied Chemistry
200 College Street, Toronto, Ontario, M5S 3E5, Canada

Abstract

It is hypothesized that the good performance of Alloy 800 in steam generator service is due to its relative immunity to two distinct mechanisms of stress corrosion cracking; the argument also applies to intergranular corrosion. One mechanism operates in the high-nickel region (Alloy 600 and nearby model alloys) and is due to internal intergranular oxidation. The other operates in the low-nickel (stainless steel) region and is due to de-alloying of Fe and/or Cr. This latter mechanism may, under special conditions, operate in high-Ni, high-Cr alloys such as 690. Some essential features of the de-alloying mechanism are demonstrated using strong caustic solutions, and the prospect of extending this approach to dilute high-temperature environments is discussed.

1. Introduction

Alloy 800 has had remarkably few corrosion problems in steam generator service. To the extent that anyone has tried to explain this, the explanations have an air of Goldilocks about them: the amounts of Fe, Ni and Cr in the alloy are 'just right'[1]. But not since 1967 has there been a scientific theory accounting for all or part of this behaviour. And those authors, Latanision and Staehle [1], abandoned their de-alloying theory because early surface-analytical studies failed to find the requisite Ni enrichment on Cl-SCC (chloride-induced stress corrosion cracking) fracture surfaces. The reasons for this were discussed by Newman and others much later [2,3].

A persuasive argument for the role of de-alloying in the SCC of austenitic stainless steels is obtained by examining their behaviour in strong caustic solutions, where the compositional dependence is known to be similar to that of Cl-SCC. It was already known from research related to AGR boilers [4] that there was a region of very fast caustic SCC of 316SS at low potential, and Deakin et al. [5,6] recently showed that this was associated with a de-alloying process in which the austenite solid solution was converted into a nanoporous metallic material with a composition approximating to 50Ni-50Fe. The de-alloyed layer is much thicker and more obvious in caustic solution because nickel cannot dissolve, whereas in acid chloride there is simultaneous dissolution of the alloy components, which keeps any de-alloyed layer thin.

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[1] On the other hand, "Someone's been sitting in my chair and they've broken it all to pieces," cried the Baby bear.

So the hypothesis for the Fe-rich region is that the essential SCC mechanism is based on de-alloying and nanoporous layer formation, leading to a film-induced cleavage or similar cracking mechanism [7].

The Ni-rich region has been more controversial and has attracted more mechanistic speculation, because of the importance of SCC of Alloy 600 in the 1980s and 1990s. Despite early misgivings in the community, the internal oxidation hypothesis of Scott [8] has been gaining ground – not so much because of the extensive work of Gendron, Newman and others [9-11] but because G.S. Was recently obtained evidence for such a mechanism [12]. Oxygen diffuses into the grain boundaries and embrittles them by forming what is usually called chromium oxide but seems to be $NiCr_2O_4$, at least for some high-temperature (400-480°C) steam/hydrogen conditions [13]. Alloy 690 forms an external Cr-rich oxide which prevents oxygen ingress; the weakness of Alloy 600, as always, is its too-low Cr content.

So our overall hypothesis is that there are two main regions of SCC on the NiCrFe ternary diagram, as shown in Figure 1. The region marked "1?" will not be discussed further here.

Hypothesis: Low-Potential Stress Corrosion Map

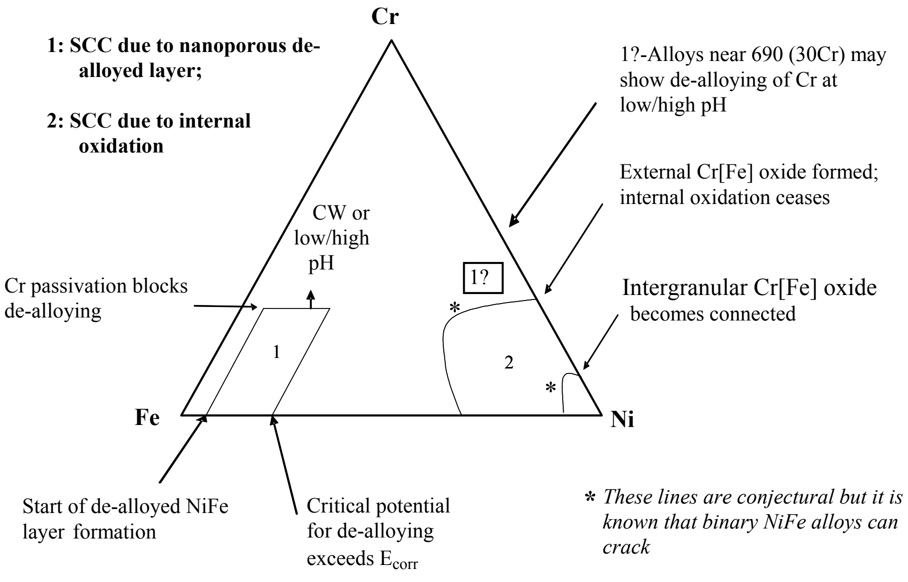


Figure 1 Hypothesis for the compositional dependence of SCC mechanisms in relatively reducing high-temperature aqueous solutions.

Since the conditions at the crack tip are relatively reducing, the overpotential for dissolution of Fe is relatively small, and above a certain Ni content the critical potential for de-alloying exceeds the corrosion potential and/or the Ni oxidation potential, thus only 'region 1' (non-porosity-forming) de-alloying will occur – Figure 2. As J.F. Newman showed [4], SCC does persist at a low rate above this potential, but probably has a different mechanism.

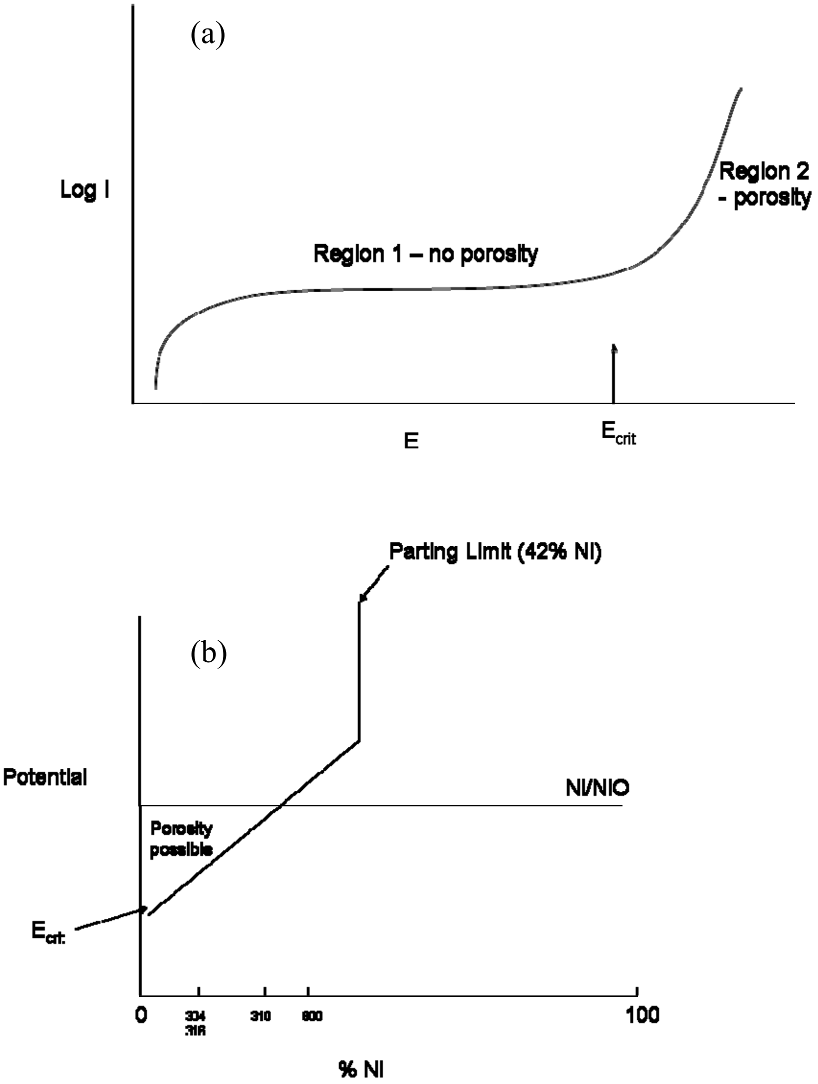


Figure 2 (a) Schematic polarization curve for a system showing de-alloying, showing regions of superficial dealloying without nanoporosity (region 1) and penetrating de-alloying with nanoporosity (region 2); (b) Interpretation of the behaviour of the Fe-Cr-Ni system on such a basis. [compositions in at.%]

The composition of 42% Ni shown on Figure 2b is an important fixed point of the system: the *parting limit*, or Ni content above which no porosity formation will occur, irrespective of how oxidizing the potential or aggressive the solution (within reason). This value is derived from studies of noble-metal alloys, and from Kinetic Monte Carlo (KMC) atomistic computer simulations [14]. Since the parting limit is affected slightly by surface diffusion of the more-noble alloy component[s], we assume that for a metal with a high melting point, like nickel, the parting limit will be close to its simulated value without diffusion. The parting limit is very close to, but not identical to, a *high-density site percolation threshold* for the fcc lattice (threshold for site percolation of active-element atoms with 9 or more like neighbours), which is 60.0% (40.0% noble-element atoms).

Figure 3 shows simulated de-alloying kinetics for an alloy whose noble metal has a surface diffusivity appropriate for gold, i.e. relatively high: the parting limit is around 54% of the active alloy component(s), i.e. 46% Au.

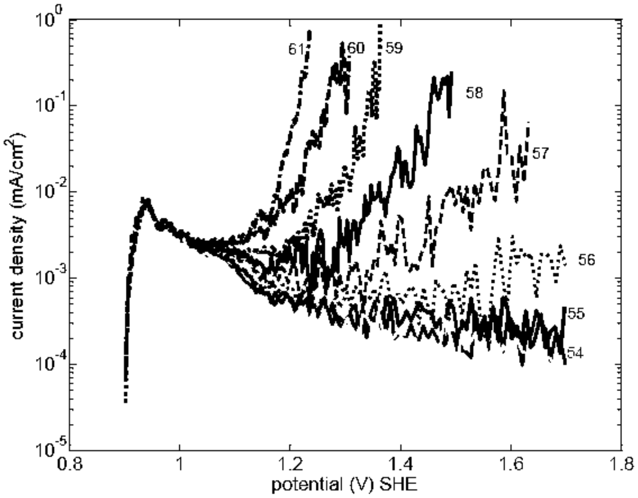


Figure 3 Simulated KMC de-alloying kinetics for a binary alloy system modelled on Ag-Au [13], showing a parting limit around 54% Ag (46% of more noble element).

Figure 4 shows the effect of reducing the surface diffusivity of the noble component by 2 orders of magnitude (this would underestimate the difference between Au and Ni), showing how the parting limit moves towards the fundamental value of 58% as the diffusivity is reduced.

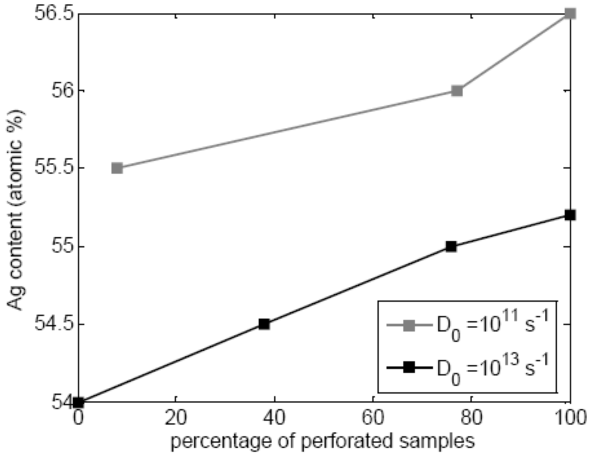


Figure 4 Statistics of multiple KMC simulations of de-alloying near the parting limit, showing the effect of lowering the surface diffusivity of the more-noble alloy component. The parting limit approaches the fundamental limit of 58% "Ag" (where "Ag" is the more active element).

2. Experimental studies of de-alloying in caustic solutions

The electrochemical procedures were similar to those used by Deakin et al. [5,6] but using a superior electrochemical cell (nickel beaker) and a PAR 2263A software-controlled electrochemical system. The reference electrode was an external Hg/HgO/20% NaOH. The NaOH concentrations used were 30% and 50% by weight, and the temperatures were 110 and 140°C. The solutions were deoxygenated with nitrogen. Various potentiodynamic and potentiostatic procedures were used, and will be described, as appropriate for each result displayed. Electrochemical impedance spectroscopy (EIS) was carried out at the open-circuit (corrosion) potential, and also at controlled electrode potentials within the de-alloying range – the main purpose of this was to detect increases in the double-layer capacitance due to nanoporous metallic layer formation (thus we plot the imaginary component of impedance rather than the magnitude in the Bode plots to be shown later). The materials used are shown in Table 1.

Table 1 Compositions and origins of the materials studied.

Material	**Source**	**%**	**Fe**	**Ni**	**Cr**	**C**	**Mn**	**Si**	**Al**	**Cu**	**Ti**
Fe	Goodfellow	wt%	99.99								
Ni	Alfa Aesar	wt%		99.5							
Fe-10Ni	Ames Lab, DOE	wt% (99.95% purity)	90	10							
Fe-10Ni-11Cr	Ames Lab, DOE	wt% (99.95% purity)	79	10	11						
310SS	Metal Samples	wt%	balance	19.28	25.32	0.06	1.72	0.54		0.1	
Alloy 800	Metal Samples	wt%	46.33	31.19	19.98	0.07	0.9	0.21	0.49	0.25	0.58

3. Results of the electrochemical study

The behaviour of basic stainless steels such as 316SS was well shown by Deakin et al. [5,6]. Exposure at the open-circuit potential in strong caustic solution (50% NaOH at 140°C) led to prolonged corrosion despite the potential being well below the Ni/NiO equilibrium potential; metallography, X-ray diffraction and EIS showed that there was a nanoporous metallic layer on the surface. The present work is focused on the behaviour of more highly Ni-alloyed materials, such as SS310 and Alloy 800, in similar solutions. Some of the preliminary results were shown in a recent paper [15].

Figure 5 shows simple voltammetry of iron, nickel and Fe-10Ni in 30% NaOH at 110°C. The Ni/NiO potential is well shown by the behaviour of pure nickel. Alloys that show a stable region of active dissolution below that potential are actually undergoing de-alloying and forming a nanoporous metallic surface layer.

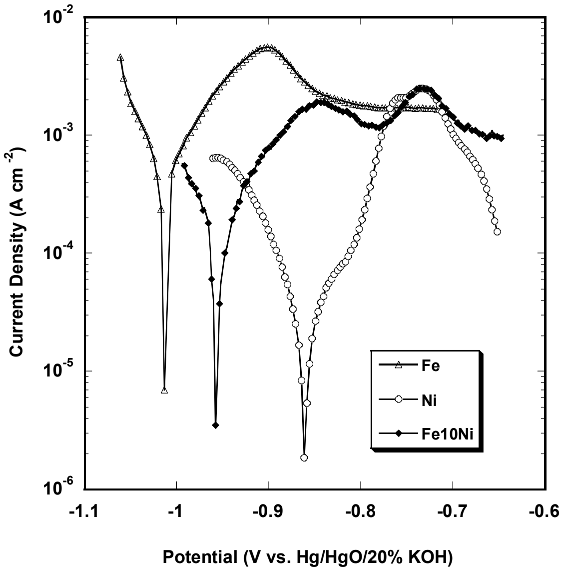


Figure 5 Anodic potential scans in 30% NaOH at 110°C of several materials, displaying the effect of alloyed nickel. Scan rate 3 mV/s.

During corrosion of the Fe-10Ni alloy, its double-layer capacitance increased dramatically as would be expected if a nanoporous layer was forming – Figure 6. This is similar to the result shown by Deakin et al. for 316SS.

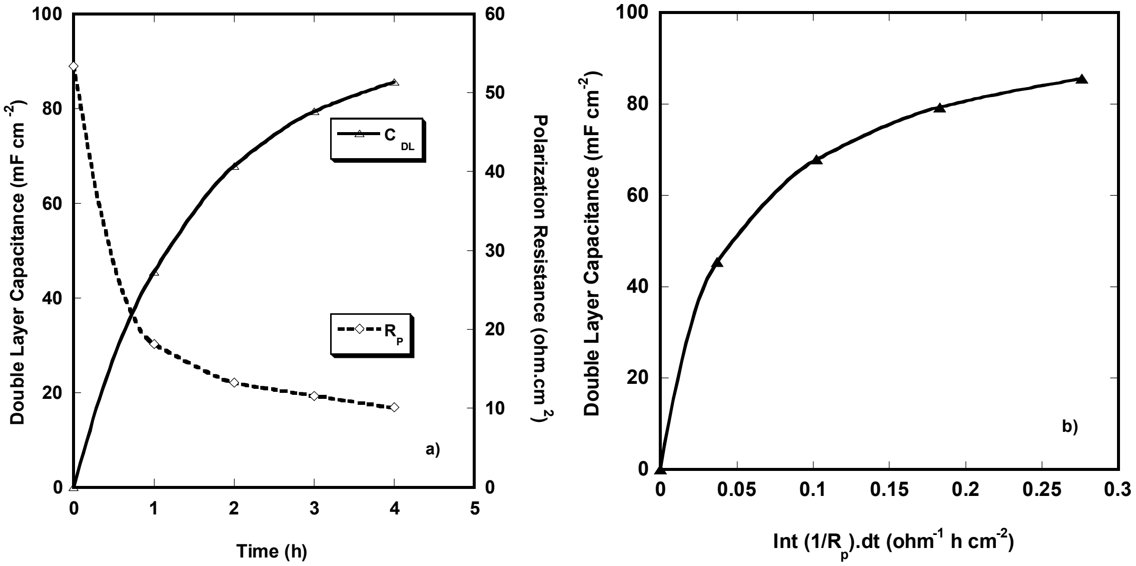


Figure 6 (a) Double layer capacitance and polarization resistance versus time and (b) the dependence of electrode capacitance on the integral of 1/R_P for Fe10Ni during exposure to 30% NaOH at 110°C for 4 h at the open circuit potential.

Type 310 stainless steel is an important intermediate material between the ordinary 300-series steels and Alloy 800. It is relatively, though not completely, resistant to Cl-SCC. It provides an ideal model system for investigating the effect of Ni content on de-alloying and SCC.

Figure 7 shows initial evidence that in 50% NaOH at 140°C, 310SS is likely to be forming nanoporosity. For potentials below the Ni/NiO potential, the current density in the flat region of the curve does not vary much with scan rate, whereas in studies of noble-metal alloys, the current density in a similar flat region decays steeply. In 30% NaOH at 110°C, similar curves showed a steady logarithmic decline in the current density in the flat region with decreasing scan rate, indicating that we are in region 1 of the de-alloying behaviour (approximately, $i \sim t^{-1}$). We conclude that it is worthwhile investigating whether the current-time behaviour in the apparently flat, 'sub-critical' region in 50% NaOH at 140°C would reveal bulk de-alloying and nanoporosity formation, with unknown kinetic factors causing the current-potential curve to be so flat compared with its noble-metal analogue.

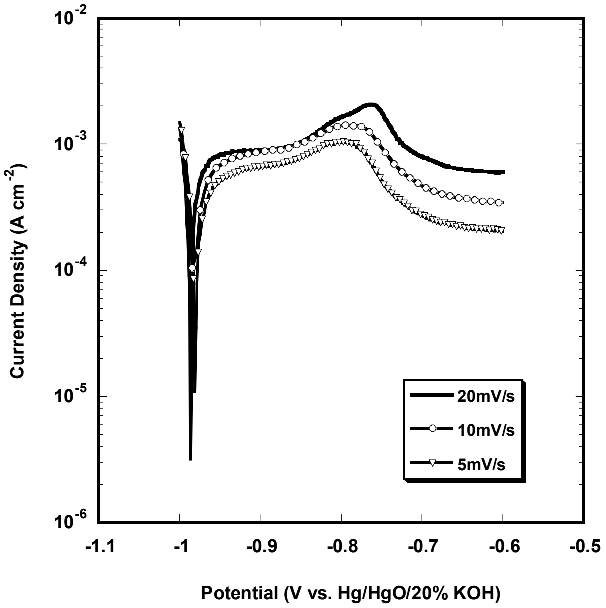


Figure 7 Anodic potentiodynamic curves recorded for 310SS in 50% NaOH at 140°C at different scan rates, showing an unusually slow decline in the current density with decreasing scan rate in the apparently subcritical region.

Current-time curves recorded at -900 mV (Hg/HgO) confirmed that 310SS was de-alloying in 50% NaOH at 140°C – Figure 8. In 30% NaOH at 110°C no such behaviour was observed.

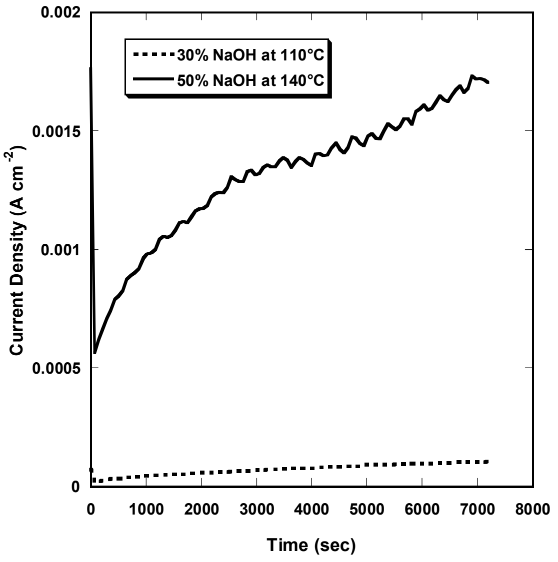
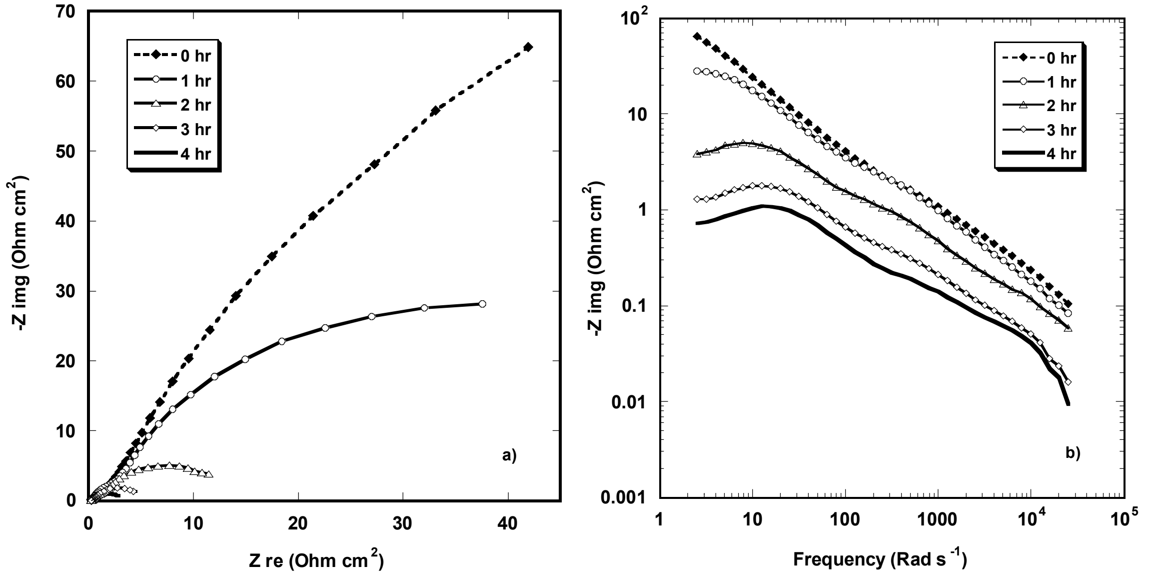


Figure 8 Current-time curves for 310SS at -900 mV (Hg/HgO) in 50% NaOH at 140°C and at -875 mV (Hg/HgO) in 30% NaOH at 110°C, showing the slow onset of de-alloying over a 2 hr immersion period in the stronger caustic solution.

EIS study of 310SS in this solution showed a clear increase in double-layer capacitance with time, indicating the formation of a nanoporous metallic layer (although the data cannot be modeled using a classical capacitance) – Figure 9.



a) b)

Figure 9 EIS data for 310SS in 50% NaOH at 140°C showing an increase in double-layer capacitance with time indicative of formation of a nanoporous layer. (a) Nyquist Plot, (b) Bode Plot of the imaginary component of impedance. Sample held at -900 mV (Hg/HgO).

Alloy 800 also showed prolonged anodic currents below the Ni/NiO potential in 50% NaOH – Figure10.

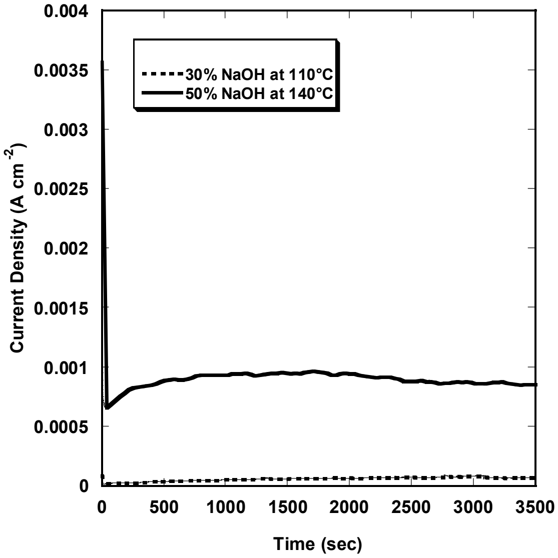


Figure 10 Current-time curves for Alloy 800 at -900 mV (Hg/HgO) in 50% NaOH at 140°C and at -875 mV (Hg/HgO) in 30% NaOH at 110°C, showing small anodic currents over a 1 hr immersion period.

However during prolonged exposure at -900 mV (Hg/HgO) in 50% NaOH at 140°C no significant increase in electrode capacitance was observed with the Alloy 800 (Figure 11).

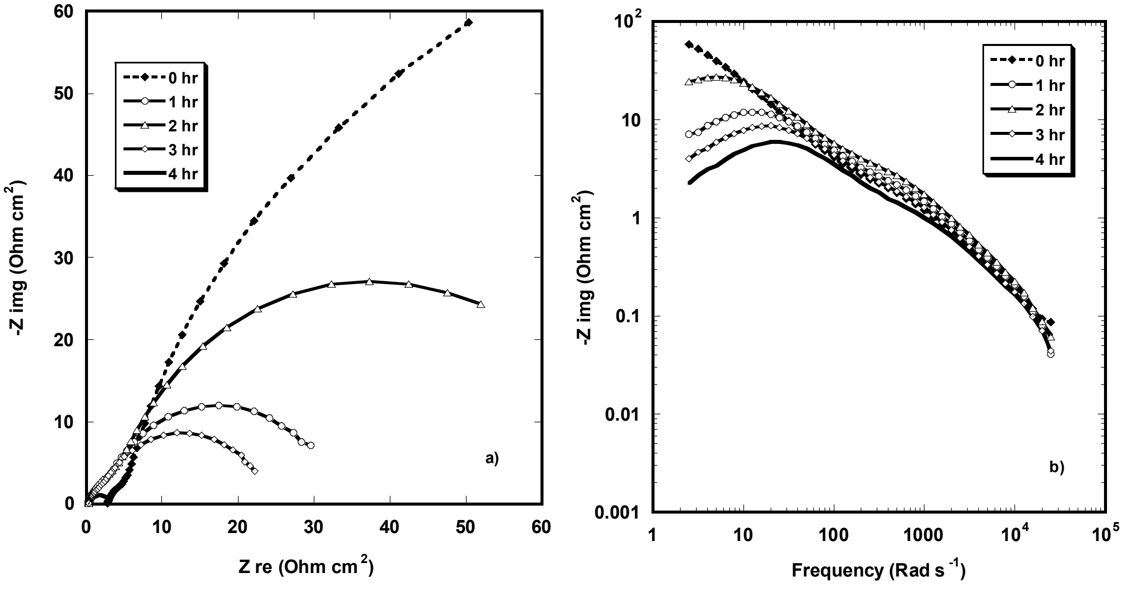


Figure 11 EIS data for Alloy 800 in 50% NaOH at 140°C showing little change in double-layer capacitance with time. (a) Nyquist Plot, (b) Bode Plot of the imaginary component of impedance. Sample held at -900 mV (Hg/HgO).

4. Further comments and conclusions

We have explored the higher-nickel region of the Fe-rich caustic SCC diagram using 310SS as the main model system. It is clearly shown that 310SS forms a nanoporous metallic layer, albeit slowly, in strong caustic solutions. So the nickel content in 310SS (19.28%) is not enough to suppress de-alloying, despite the relatively small overpotential for Fe dissolution. The situation with Alloy 800 is less clear. There is a prolonged anodic current below the Ni/NiO equilibrium potential, but as yet no surface area increase has been observed indicative of nanoporous metallic layer formation. This is consistent with the limited susceptibility of Alloy 800 to caustic SCC. But on a dynamically straining surface, or at longer times in static exposures, one may expect some de-alloying and porosity formation, given the borderline nature of the short-term response of Alloy 800 in the solution we have investigated. Surface analysis is in progress.

Should we draw any practical conclusions from this research? We believe that Alloy 800 is very nearly immune to a range of SCC phenomena in high-temperature aqueous solutions, for the following reasons:

1 The Ni content, at around 33%, is close to the parting limit of 42% that gives unconditional immunity to de-alloying and de-alloying-related SCC.
2 Extreme chemistry, as in the present work, is required for the rather negative open-circuit potential to exceed the critical potential for de-alloying.
3 Strong caustic solutions are probably less severe than likely practical environments of near-neutral pH.

However, it would be more comforting if a new 800X alloy were developed with, say, 40 or 42% Ni.

5. Acknowledgements

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