MSE 112

2nd Mid-Term EXAM, SPRING 2006

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The use of books or notes during the Exam is NOT permitted.

ALL WORK IS TO BE DONE IN THIS BOOKLET. YOU MAY USE THE BACKS OF PAGES

All voltages are measured with respect to SHE.

Logs are in base 10 (except where noted otherwise).

1 Joule = 1 volt•coulomb = 0.239 calorie

R=gas constant = 1.9872 cal/(mole°K)

F= Faraday's Constant ≈ 96,500 coulombs/equivalent

T = temperature = 25°C (except where noted)

Problem	*Point Value*
1	55
2	20
3	25

1. This problem concerns the selection of material for a pipeline that will transport sea-water from the coast to a desalination plant. The pipeline must be resistant to pitting corrosion and must exhibit a uniform corrosion rate below $1.5\text{x}10^{-4}$ mm/yr.

A binary Fe-Cr alloy that contains 10% Cr is available for purchase at a very inexpensive price. The alternative material is 304 stainless steel, which contains 18% Cr – 10% Ni, and is considerably more expensive than the Fe-10Cr binary alloy.

At very little cost, it is possible to de-oxygenate the sea-water in the pipeline, if such deaeration can improve the corrosion performance of the pipeline.

The preferred material is the alloy that meets the performance objectives at the lower cost. Based on the information provided below, indicate (a) which alloy you would recommend for the pipeline and (b) whether or not the water should be deaerated.

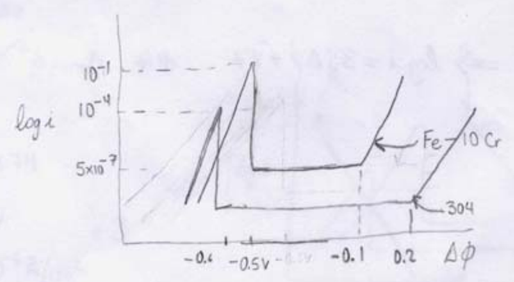
For both Fe-10Cr and 304 stainless steel, the kinetics of the reduction reactions in air-saturated sea-water (pH=8) and in deoxygenated sea-water (pH=8) are specified as follows:

	Exchange current density	slope
Air-saturated sea water	10^{-14} amps/cm^2	-1 decade/0.1V = -10
De-oxygenated sea-water	10^{-7} amps/cm^2	-1 decade/0.1V = -10

The oxidation kinetics of the two alloys in sea water are specified as follows:

max active dissolution rate →	i_{max} (amps/cm^2)	Potential of i_{max}	Slope of active region	$i_{passive}$ (amps/cm^2)	Pit Potential
Fe-10Cr	10^{-1}	-0.5V	+3.5 dec/0.1V (35dec/V)	$5\text{x}10^{-7}$	-0.1V
304 stainless steel	10^{-4}	-0.6V	+3.5 dec/0.1V (35dec/V)	$2\text{x}10^{-7}$	+0.2V

In addition, both alloys have the same molecular weight of 55.4 g/M and density of 7.9 g/cc.



$H_2: \; 2H^+ + 2e^- \rightarrow H_2$

$$\Delta\phi_e = 0 - \frac{0.0592}{2}\log\frac{P_{H_2}^{\,1}}{[H^+]^2} = 0 - 0.0592pH = -0.0592(8)$$

$$= -0.4736V$$ +5

$i_0 = 10^{-7}\ A/cm^2 \qquad m = -10$

$O_2: \; H_2O + \tfrac{1}{2}O_2 + 2e^- \rightarrow 2(OH^-) \qquad \Delta\phi_e^\circ = 0.401$

$$\Delta\phi_e = 0.401 - \frac{0.0592}{2}\log\frac{[OH^-]^2}{[H_2O]P_{O_2}^{1/2}} = 0.401 - \frac{0.0592}{2}\log\frac{[10^{-6}]^2}{0.2^{1/2}} = 0.746V$$ +5

$i_0 = 10^{-14}\ A/cm^2 \qquad m = -10$

$y = mx + b$

$\log(10^{-7}) = (-10)(-0.4736) + b \implies \log i = -10\Delta\phi - 11.74$ +4

$b = -11.74$

$\log(10^{-14}) = (-10)(0.746) + b \implies \log i = -10\Delta\phi - 6.54$ +4

$b = -6.54$

Fe − 10 Cr

$\log i = 35\Delta\phi + b$

$\log(10^{-1}) = 35(-0.5) + b \implies \log i = 35\Delta\phi + 16.5$ +4

$b = 16.5$

304 S.S

$\log i = 35\Delta\phi + b$

$\log(10^{-4}) = 35(-0.6) + b \implies \log i = 35\Delta\phi + 17$ +4

$b = 17$

@ passivation potential :

Fe-10Cr : H_2 : $\log i = -10(-0.5) - 11.74$

$i = 1.82 \times 10^{-7} < i_{max} \Rightarrow$ in active region

O_2 : $\log i = -10(-0.5) - 6.54$

$i = 2.88 \times 10^{-2}$

<u>Fe-10Cr</u>

H_2: $\log 5\times10^{-7} = -10(\Delta\phi) - 11.74$

$\Delta\phi = -0.544V < \Delta\phi_{pass}$ +2

O_2: $\log 5\times10^{-7} = -10(\Delta\phi) - 6.54$

$\Delta\phi = -0.024V > \Delta\phi_{pass}$ +3

but also greater than $\Delta\phi_{pit}$ +2

<u>304 S.S.</u>

H_2: $\log 2\times10^{-7} = -10\Delta\phi - 11.74$

$\Delta\phi = -0.504V$ +2

O_2: $\log 2\times10^{-7} = -10\Delta\phi - 6.54$

$\Delta\phi_{pit} > \Delta\phi = 0.0159V > \Delta\phi_{pass}$ +3 +2

<u>Fe-10Cr</u>

$35\Delta\phi + 16.5 = -10\Delta\phi - 11.74$

$\Delta\phi_{corr} = -0.628V$

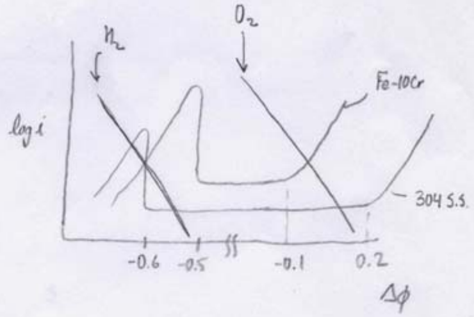
$i_{corr} = 3.43\times10^{-6} A/cm^2$ +3

<u>304 S.S.</u>

$35\Delta\phi + 17 = -10\Delta\phi - 11.74$

$\Delta\phi_{corr} = -0.639V$ +3

$i_{corr} = 4.43\times10^{-6} A/cm^2$



Reasoning +4

$1.5 \times 10^{-4}\ mm/yr \longrightarrow i \ [=]\ A/cm^2 = C/cm^2 \cdot s$

$\rho = 7.9\ g/cm^3 \quad M = 55.4\ g/mol$

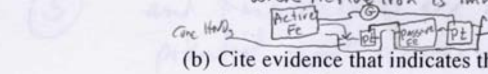
$$\frac{1.5\times10^{-5}\ cm}{yr} \times \frac{1\ yr}{365\ days} \times \frac{1\ day}{24\ hours} \times \frac{1\ hr}{3600\ s} \times \frac{7.9\ g}{cm^3} \times \frac{1\ mol}{55.4\ g} \times \frac{96{,}485\ C}{1\ eq} \times \frac{3\ eq}{1\ mol} = 1.962\times10^{-8}\ A/cm^2$$

+5

2. Answer the following questions regarding the passive film formed on iron in an aqueous borate buffer (pH=8.4). This topic was addressed in lecture and in the course notes.

   (a) What is the evidence for the good electron conductivity of iron's passive film? either: (1) The high rate of electrochemical reduction of O_2 on the surface of passive iron indicates e^-s are moving through the passive film

   or: (2) Faraday's experiment in which e^-s flow through the external circuit when Active iron is immersed in concentrated nitric acid in the following cell



(5)

   (b) Cite evidence that indicates the rate determining step in the growth of iron's passive film is the migration of iron ions through the passive film.

   The addition of Fe^{++} to the electrolyte increases the oxidation rate in the passive state and increases the thickness of the passive film.

(4)

   (c) Cite at least two pieces of evidence that indicates the passive film of iron consists of two layers.

   (i) Measurement of potential during galvanostatic cathodic polarization of passive iron exhibits three potential-arrests. The last potential arrest is due to the reduction of H^+ in the electrolyte. The other two potential arrests are due to the cathodic reduction of the two components of the passive film.

   (ii) SERS during galvanostatic cathodic reduction of passive iron indicates outer layer of passive film is an unknown Fe(III) compound and the inner layer is Fe_3O_4.

   (iii) Calculation of $\Delta\Phi_{pass}$

   (iv) TEM images

   (v) Measurement of [Fe]

(6)

   (d) Explain why the thickness of iron's passive film increases with increasing potential.

   RDS in growth of passive film is migration of Fe^{+3} through the film. When the potential is increased, the electric field through the film is increased. The higher electric field increases the rate of migration of Fe^{+3}. Increasing the rate of the RDS of film growth increases the film's thickness.

(5)

(5)

3. (a) List the different possible mechanisms of initiation of pitting corrosion of 304 stainless steel (18Cr-8Ni) in air-saturated sea water.

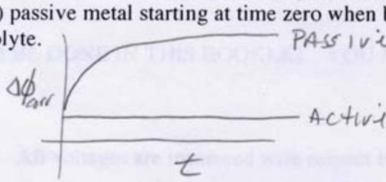
(1) Adsorption of Cl^- forms a critical size cluster of Cl_n^-, which extracts Fe^{+3} from the passive film.
(2) Adsorption of Cl^- on passive film at defects (screw dislocations, grain boundaries) in the metal
(3) Adsorption of Cl^- at defects in passive film on metal adjacent to insoluble inclusions
(4) Dissolution of soluble inclusions such as MnS. (5) Dissolution of S segregated to grain boundaries

(5)

(b) Explain why there is often considerable scatter in the measured value of an alloy's pitting potential. Pitting potential is the potential at which a pit initiates at the worst defect in the alloy. The types of defects are listed in 3(a) and these defects are not very reproducible*, hence the pitting potential is not reproducible. (*e.g., the composition, size and shape of soluble inclusions, such as MnS, are not reproducible).

(4)

(c) Make a sketch of the variation of corrosion potential with time of an (i) active metal and a (ii) passive metal starting at time zero when both alloys are immersed into the electrolyte.



(6)

(d) Describe two tests that you would use to determine the relative susceptibilities of five different alloys to crevice corrosion in sea-water.

(1) Affix teflon crevices to a large number of samples and measure the fraction of samples that exhibit crevice corrosion after 1 month in sea water.
(2) Determine the nature and extent of changes in the anodic polarization curves when the solution is changed from 0.1M NaCl to 1M HCl

(5)

(e) The nominal composition (expressed as weight percent) of 304 stainless steel consists of 18% Cr, 8% Ni, 1% Mn, 1% Si, ≤0.08 % C. (i) Indicate the main reason for the presence of each element. (ii) List compositional changes that would increase the resistance of 304 stainless steel to sensitization.

Cr – to decrease passivation potential and to decrease corrosion rate in the passive state

Ni – to stabilize the fcc crystal structure

Mn – to tie up sulfur (by forming MnS).

Si – to lower the steel's oxygen concentration.

C – to increase strength.