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## STRESS CORROSION CRACKING BEHAVIOR OF ALLOY 22 IN MULTI-IONIC AQUEOUS ENVIRONMENTS

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### ABSTRACT

The US Department of Energy is characterizing a potential repository site for nuclear waste in Yucca Mountain (NV). In its current design, the nuclear waste containers consist of a double metallic layer. The external layer would be made of N06022 or Alloy 22 (Ni-22Cr-13Mo-3W-3Fe). Since over their lifetime, the containers may be exposed to multi-ionic aqueous environments, a potential degradation mode of the outer layer could be environmentally assisted cracking (EAC) or stress corrosion cracking (SCC). In general, Alloy 22 is extremely resistant to SCC, especially in concentrated chloride solutions. Current results obtained through slow strain rate testing (SSRT) shows that Alloy 22 may suffer SCC in simulated concentrated water (SCW) at applied potentials approximately 400 mV more anodic than the corrosion potential ( $E_{\text{corr}}$ ).

### INTRODUCTION

If water is present, there are three types of corrosion degradation modes that may occur in the containers. These are: (1) General or uniform corrosion, (2) Localized corrosion and (3) Environmentally assisted cracking (EAC). (Figure 1 outlines what corrosion modes are considered and what can affect these corrosion modes.)

Mill annealed Alloy 22 is highly resistant to SCC in acidic concentrated chloride solutions.<sup>1-5</sup> Dunn et al. did not find SCC when they tested Alloy 22 in 14 molal  $\text{Cl}^-$  (as  $\text{MgCl}_2$ ) at 110°C and 9.1 molal  $\text{LiCl}$  at 95°C under controlled potential.<sup>1-3</sup> They used wedge opening loaded double cantilever beam (DCB) and compact tension (CT) specimens at stress intensities in the range 32 to 47  $\text{MPa}\cdot\text{m}^{1/2}$  for times as long as 52 weeks.<sup>1-3</sup> Rebak reported that Alloy 22 U-bend specimens did not suffer SCC when exposed to 45%  $\text{MgCl}_2$  at 154°C for up to 6 weeks.<sup>4</sup> Estill et al. performed SSRT at a  $1.6 \times 10^{-6} \text{ s}^{-1}$  strain rate at the corrosion potential ( $E_{\text{corr}}$ ) in 4 M  $\text{NaCl}$  at 98°C, saturated  $\text{CaCl}_2$  (>10 M  $\text{Cl}^-$ ) at 120°C and 1%  $\text{PbCl}_2$  at 95°C.<sup>5</sup> None of these specimens showed a loss of ductility or secondary cracking<sup>5</sup> (Table 1).

Even though Alloy 22 is resistant to SCC in concentrated chloride solutions, it may be susceptible under other severe environmental conditions.<sup>6-9</sup> Andresen et al. tested the susceptibility of Alloy 22 to EAC at the corrosion potential ( $E_{\text{corr}}$ ) in basic saturated water (BSW) at 110°C.<sup>6</sup> This BSW multi-ionic solution is a version of concentrated solutions that might be obtained after evaporative tests of Yucca Mountain ground waters.<sup>6</sup> Using the reversing DC potential drop technique, Andresen et al. reported a crack grow rate of  $5 \times 10^{-13} \text{ m/s}$  in a 20% cold-worked specimen loaded to a stress intensity of 30  $\text{MPa}\cdot\text{m}^{1/2}$ . This EAC testing was carried out in air saturated BSW water of pH ~ 13. The testing conditions used by Andresen et al. were highly aggressive and, in spite of that, the measured

crack growth rate was near the detection limit of the system.<sup>6</sup> Rebak et al. reported that Alloy 22 U-bend specimens suffered transgranular SCC when they were exposed for 336 h to aqueous solutions of 20% HF at 93°C and to its corresponding vapor phase<sup>7</sup> (Table 1). The liquid phase was more aggressive than the vapor phase.<sup>7</sup> Pulvirenti et al. reported transgranular cracking in one out of four Alloy 22 U-bend specimen exposed for 15 days at 250°C in concentrated ground water contaminated with 0.5 % lead (Pb) and acidified to pH 0.5<sup>8-9</sup> (Table 1). Estill et al. performed slow strain rate tests, cyclic loading tests and U-bend tests in large variety of environments (temperature, applied potential and solution composition).<sup>5</sup> They only reported SCC on MA Alloy 22 through SSRT in saturated concentrated water (SCW) at 73°C and at a potential of +0.4V [SSC].<sup>5</sup>

## EXPERIMENTAL TECHNIQUE

The material for the specimen was prepared from plate stock, Heat 2277-8-3126

The chemical composition of the alloy in weight percent was: ~57% Ni, 21.7% Cr, 13.26% Mo, 2.8% W, 3.59% Fe, 1.03% Co, 0.27% Mn, 0.14% V, 0.004% C and 0.001% S

The typical mechanical properties of MA plate material are listed in Table 2.

Each specimen was cylindrical, approximately 7.25-inch (184 mm) long and 0.438-inch (11 mm) diameter. The useful gage of the specimens was 1-inch (25.4 mm) long and had a 0.1-inch (2.54 mm) diameter. The slow strain rate tests were conducted at a constant deformation rate of  $1.6 \times 10^{-6} \text{ s}^{-1}$ . The concentration of some testing solutions are given in Table 3. The apparatus set up is shown in Figure 2.

## EXPERIMENTAL RESULTS AND DISCUSSION

Table 4 shows the experimental results in SCW. Two specimens were strained to rupture in air as reference tests for inert environments. Table 4 shows the testing conditions such as testing temperature, applied potential and  $E_{\text{corr}}$  of the specimens in the solution before the tests. The average  $E_{\text{corr}}$  of all the specimens (Table 4) before starting the applied potential was approximately -0.15 V in the saturated silver chloride scale [SSC] which at room temperature is approximately 200 mV more positive than the normal hydrogen electrode [NHE].

Figure 3 shows the time to failure of the strained specimens as a function of the applied potential. Figure 3 shows that the higher the applied potential the lower the time to failure. The lowest time to failure was obtained for the specimens strained at +0.4 V [SSC]. Figure 4 is an SEM image of the fracture end of a specimen strained in air. This shows typical ductile failure with necking before cracking. Figure 5 shows a SEM low magnification image of a specimen strained in SCW at +0.1 V [SSC] and Figure 6 is a larger magnification of the lateral surface of the same specimen. Alloy 22 was not susceptible to cracking at +0.1 V [SSC] since the specimen showed considerable necking before failure (Figure 5) and the lateral surface was free of secondary cracking (Figure 6). Figures 7-8 show the characteristics of a specimen strained in SCW at +0.2 V [SSC]. Figure 7 shows considerable necking before failure; however, Figure 8 shows incipient secondary cracking in the lateral surface. Figure 9 is a low magnification SEM image of a specimen strained in SCW at +0.4 V [SSC] showing that the failure of this specimen occurred with little reduction in area (necking). Figure 9 also shows that there is abundant secondary cracking in the lateral surface. Figure 10 is an SEM image of the fracture surface showing that the environmentally induced cracking was transgranular in nature. Figure 11 is a metallographic cross section of the same specimen showing that

the EAC cracks are shallow and open, probably because the strain rate was high; not allowing enough time for crack propagation.

Figure 12 shows the stress-elongation curves for Alloy 22 specimens strained at 0.4 V in three different electrolyte solutions. Figure 12 shows that Alloy 22 was susceptible to EAC in SCW solution at 73°C but was not susceptible to EAC in basic saturated water (BSW) pH 12 at 105°C or simulated saturated water (SSW) pH 6.7 at 100°C. Table 4 shows that when Alloy 22 was strained in SCW at +0.4 V [SSC] at ambient temperature (25°C), the parameters time to failure, ultimate tensile strength and reduction in area were similar to the same parameters for the specimens strained in air.

Figure 13 shows the polarization curve for MA Alloy 22 in SCW at 90°C. There is an anodic peak in the potential range between +0.2 to +0.4 V [SSC]. The range of potential for cracking susceptibility of Alloy 22 seems to be associated to the presence of this anodic peak.

Current results show that for MA Alloy 22 to fail by EAC in SCW solution, several conditions are required to be applied simultaneously: (1) A temperature higher than approximately 70°C, (2) A stress level in the order of 600 MPa (two times the level of the yield stress) and (3) Anodic potentials in the order of +0.3 V [SSC]. Therefore, it is unlikely that the actual container would be susceptible to EAC even though it may enter in contact with a SCW type of solution at high temperature. Firstly, because in the design of the waste package it is predicted that the container will be fully annealed to eliminate any residual stress due to welding. Second, because data (Figure 14) shows that the  $E_{\text{corr}}$  of Alloy 22 after more than 5 years immersion in aerated SCW at 90°C remained below 0 V [SSC], that is, at least 0.3 V below the range of potential susceptibility. Table 2 also shows that  $E_{\text{corr}}$  for Alloy 22 in aerated SCW was also below 0 V [SSC].

## CONCLUSIONS

- (1) Alloy 22 is resistant to EAC or SCC in concentrated chloride solutions.
- (2) Alloy 22 is resistant to EAC in most multi-ionic solutions simulating concentrated underground waters.
- (3) Alloy 22 was susceptible to EAC in SCW at +0.3 and +0.4 V [SSC] at temperatures 73-89°C. However, EAC did not occur at +0.4 V and 25°C.
- (4) It is unlikely that Alloy 22 would suffer EAC under environmental conditions that could be encountered in Yucca Mountain since the stresses of the container will be relieved and because  $E_{\text{corr}}$  of the alloy is expected to be below the potential range for susceptibility.

## ACKNOWLEDGMENTS

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PREVIOUS WORK  
SUSCEPTIBILITY OF ALLOY 22 TO STRESS CORROSION CRACKING

Reference	Tested Conditions	SCC?
Dunn et al. [1-3]	Wedge opening loaded double cantilever beam (DCB) and compact tension (CT) specimens at stress intensities in the range 32 to 47 MPa.m <sup>1/2</sup> for times as long as 52 weeks in 14 molal Cl <sup>-</sup> (as MgCl <sub>2</sub> ) at 110°C and 9.1 molal LiCl at 95°C under controlled potential.	No
Rebak [4]	U-bend specimens exposed to 45% MgCl <sub>2</sub> at 154°C for up to 6 weeks.	No
Estill et al. [5]	SSRT at a 1.6 x 10 <sup>-6</sup> s <sup>-1</sup> strain rate at the corrosion potential (E <sub>corr</sub> ) in 4 M NaCl at 98°C, saturated CaCl <sub>2</sub> (>10 M Cl <sup>-</sup> ) at 120°C and 1% PbCl <sub>2</sub> at 95°C	No
Estill et al. [5]	SSRT in Multi-ionic Solutions Simulating Concentrated Underground Water such as BSW and SSW at 100°C and +400 mV [SSC]	No
Rebak et al. [7]	U-bend specimens exposed for 336 h to aqueous solutions of 20% HF at 93°C and to its corresponding vapor phase.	Yes
Pulvirenti et al. [8-9]	U-bend specimen exposed for 15 days at 250°C in concentrated ground water contaminated with 0.5 % lead (Pb) and acidified to pH 0.5	Yes

TABLE 2  
TYPICAL MECHANICAL PROPERTIES OF PLATE AND SHEET ALLOY 22

Heat	Tensile Strength [UTS] (MPa)	Yield Stress [0.2%] (MPa)	Elongation to Rupture (%)	Hardness (RB)	ASTM Grain Size
Sheet – 2277- 8-3203	824	412	62	92	5.5
Plate – 2277-8- 3126	766	387	64.4	83	4

TABLE 3

CONCENTRATION OF TYPICAL UNDERGROUND WATERS IN mg/L

Ion	J-13 Well Water pH 7.4	Unsaturated Zone (UZ) Pore Water pH 5.6	Simulated Concentrated Water (SCW) pH 10.3	Simulated Saturated Water (SSW) pH 6.7	Basic Satu- rated Water (BSW) pH 13
K <sup>+</sup>	5.04	0.01	3400	141,600	81,480
Na <sup>+</sup>	45.8	9	40900	487,000	231,225
Mg <sup>2+</sup>	2.01	12	< 1	---	---
Ca <sup>2+</sup>	13	65	< 1	---	---
F <sup>-</sup>	2.18	0	1400	---	1616
Cl <sup>-</sup>	7.14	77	6700	128,000	169,204
NO <sub>3</sub> <sup>-</sup>	8.78	12	6400	1,313,000	177,168
SO <sub>4</sub> <sup>2-</sup>	18.4	79	16700	---	16,907
HCO <sub>3</sub> <sup>-</sup>	128.9	66	70000	---	107,171
SiO <sub>3</sub> <sup>2-</sup>	61.1	46	~ 40	---	9038

TABLE 4  
SLOW STRAIN RATE ( $\sim 1.6 \times 10^{-6} \text{ S}^{-1}$ ) TESTING OF MA ALLOY 22 IN SCW

Sample	Temp. (°C)	E <sub>corr</sub> (mV, SSC)	E <sub>applied</sub> (mV, SSC)	Time to Failure (h)	UTS (ksi)	RA (%)	Observations Stereomicroscope X 40 and X100
012 (Air)	22	NA	NA	124	114	74	Ductile, Necking
040 (Air)	22	NA	NA	123	118	70	Ductile, Necking
026	73	-241	+100	120	111	79	Ductile Failure, neck- ing. No SCC
023	73	-224	+200	NA	NA	72	Necking. Incipient or Shallow SCC
025	73	-172	+200	116	NA	80	Necking. Incipient or Shallow SCC
029	88.5	-144	+200	112	NA	73	Necking. Incipient or Shallow SCC
030	73	-182	+300	98	NA	65	SCC
021	73	-171	+400	90	96	64	SCC
112	95	-94	+400	91	101	71	SCC
033	86	-169	+400	76	NA	44	SCC
020	25	-109	+400	116	114	85	Ductile Failure, neck- ing. No SCC

RA: Reduction in area at time of rupture, NA = Not Applicable or Not Available. For many samples the UTS value was not recorded during testing, that is, the data is not available.

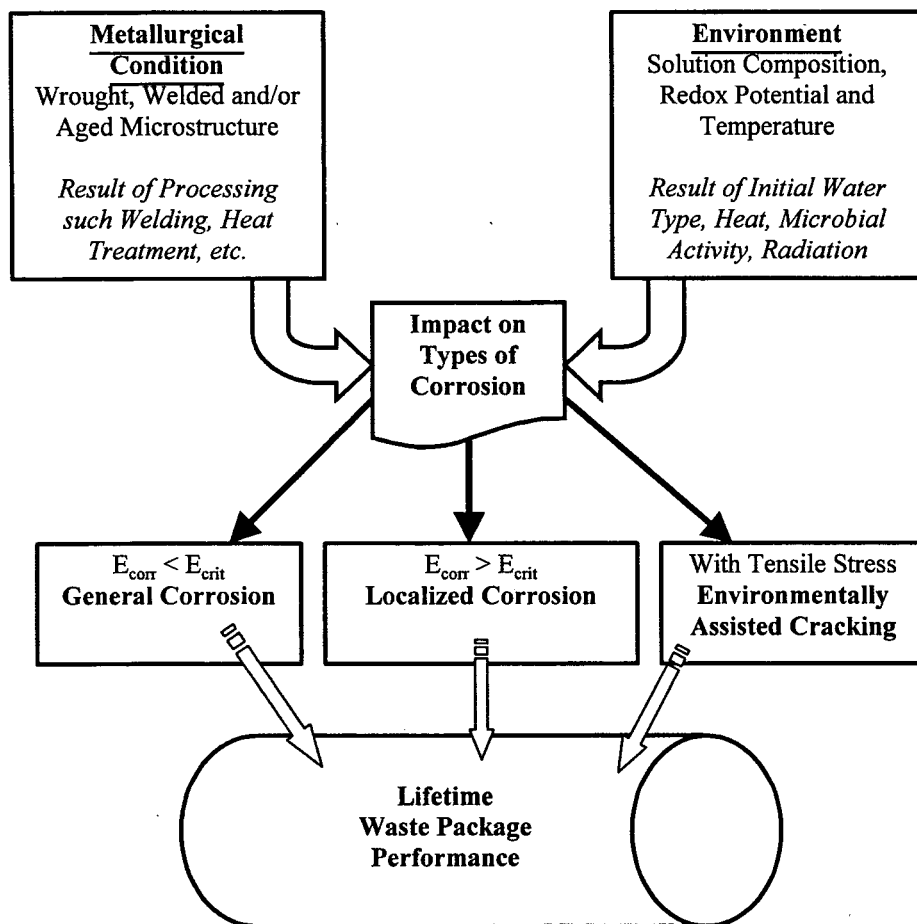


FIGURE 1: General Model For Corrosion Degradation of Alloy 22

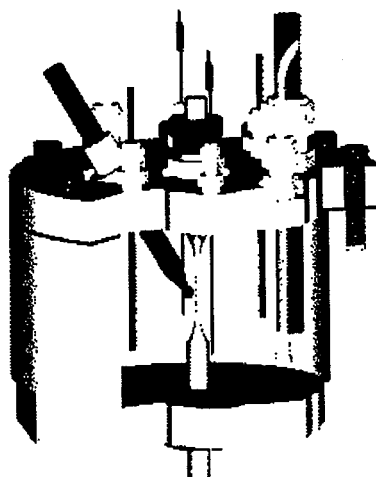


Figure 2: Apparatus Set Up for SSRT Testing

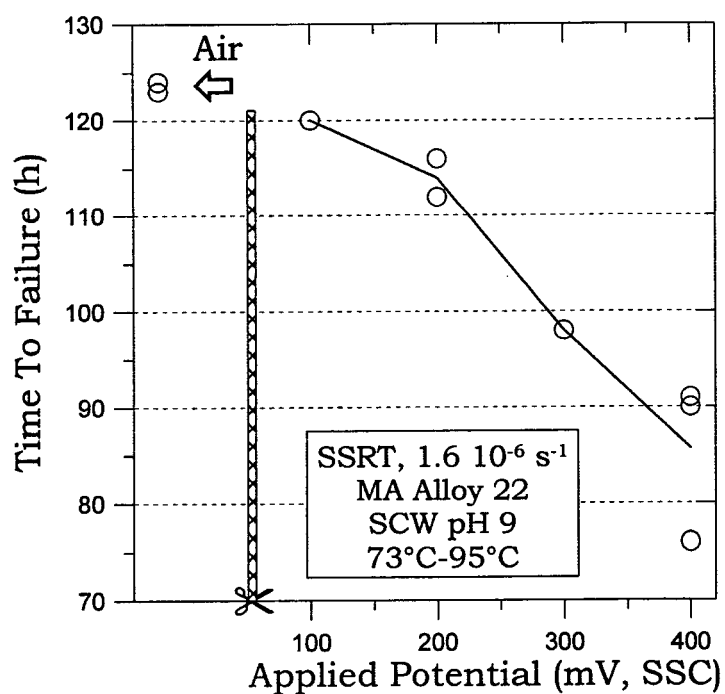


FIGURE 3: Effect of Potential on the time to failure of Alloy 22 in SCW.



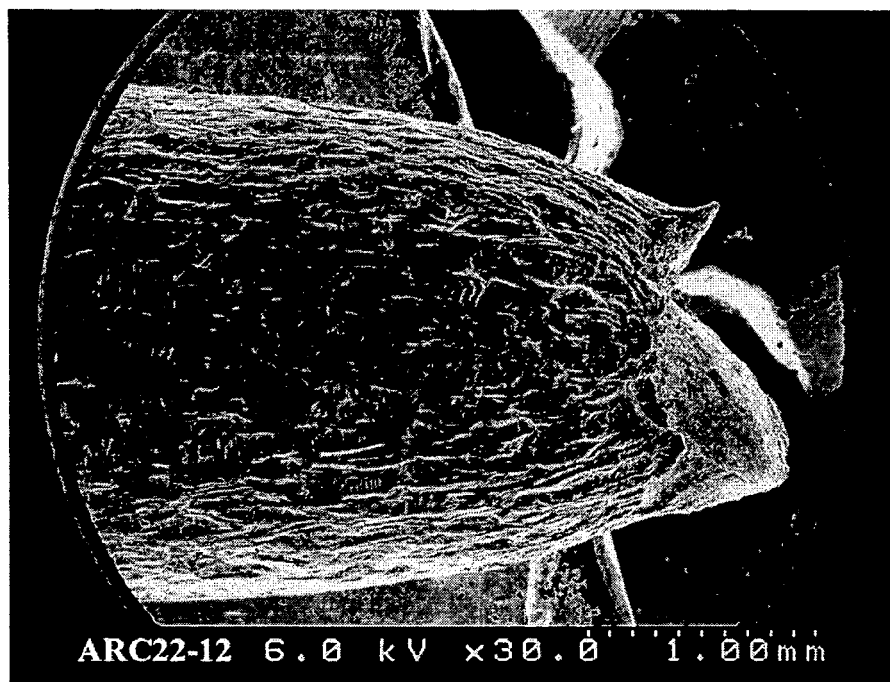


FIGURE 4: Fracture end of specimen strained in air at ambient temperature.  
Magnification X 30.

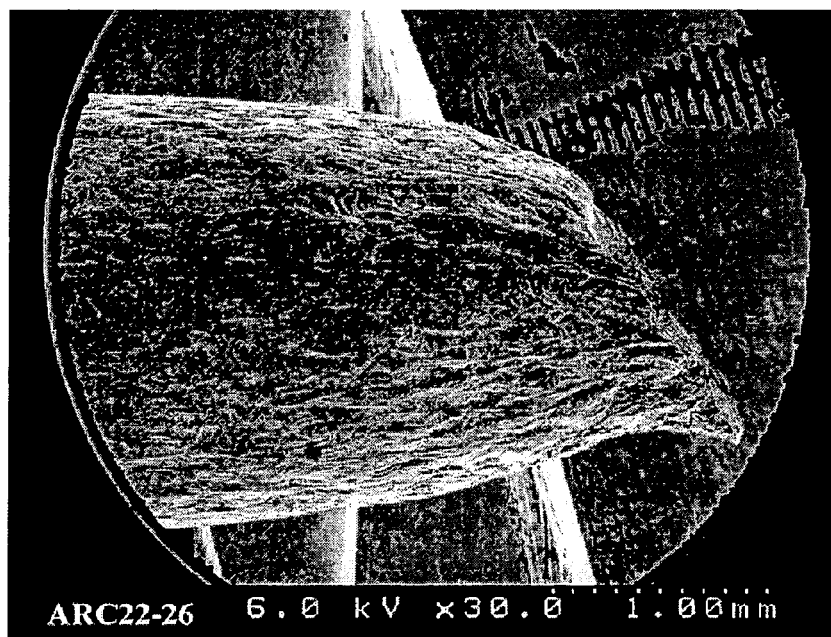


FIGURE 5: Fracture end of specimen strained in SCW at 73°C and +0.1 V.  
Magnification X 30.



FIGURE 6: Fracture end of specimen strained in SCW at 73°C and +0.1 V.  
Magnification X 500.



FIGURE 7: Fracture end of specimen strained in SCW at 73°C and +0.2 V.  
Magnification X 30.

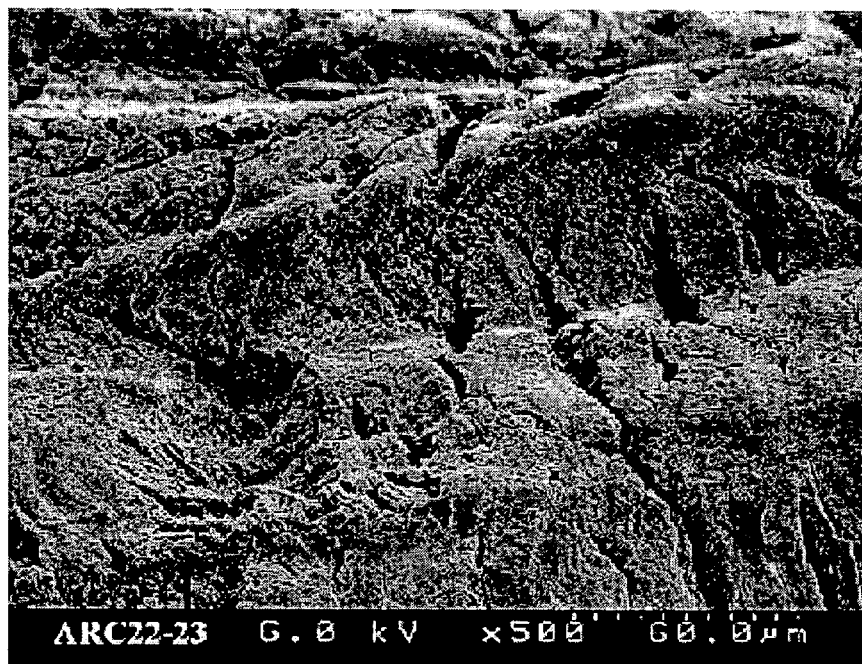


FIGURE 8: Fracture end of specimen strained in SCW at 73°C and +0.2 V.  
Magnification X 500.

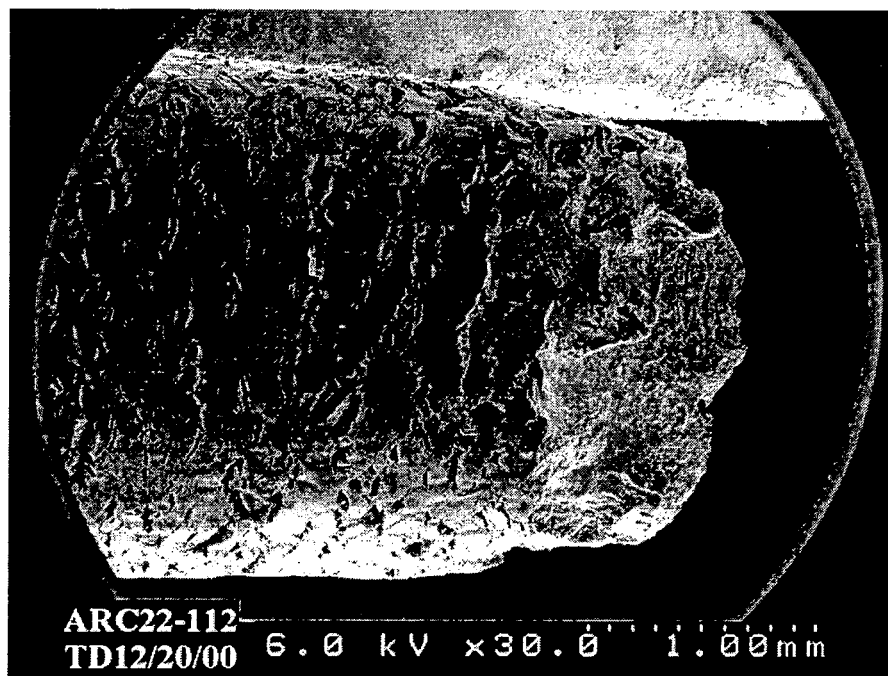


FIGURE 9: Fracture end of specimen strained in SCW at 73°C and +0.4 V.  
Magnification X 30.

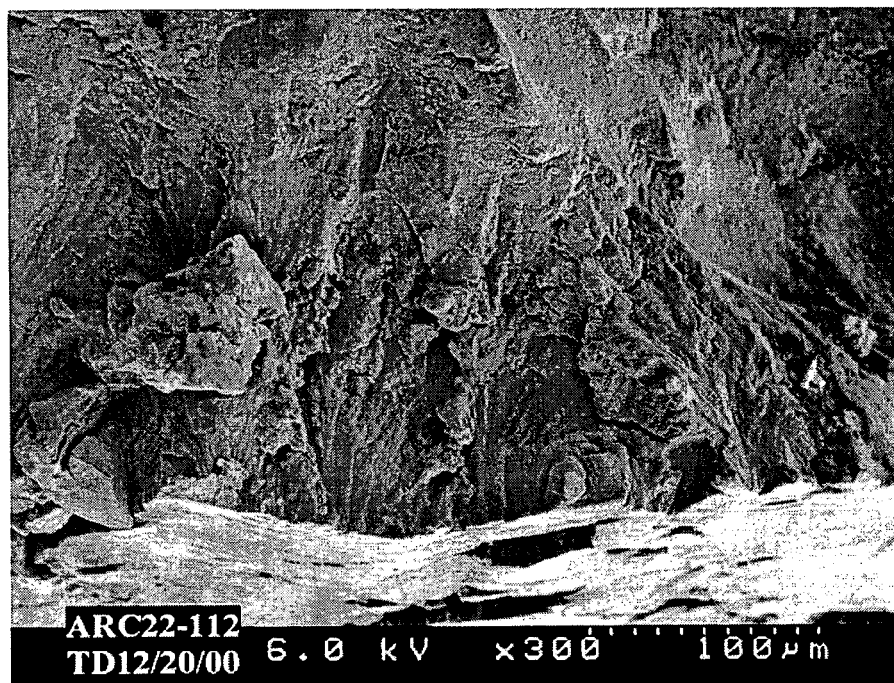


FIGURE 10: Fracture surface of specimen strained in SCW at 73°C and +0.4 V.  
Magnification X 300.

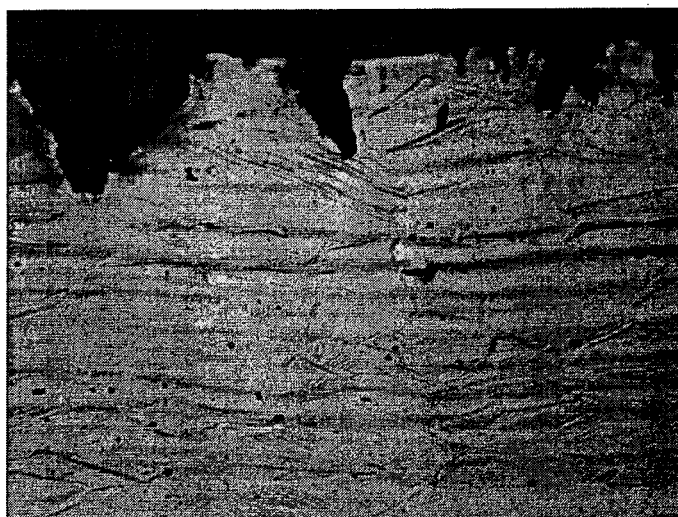


FIGURE 11: Metallographic sectioning of Alloy 22 (112) strained in SCW at 73°C and +0.4 V.  
Magnification X 200.

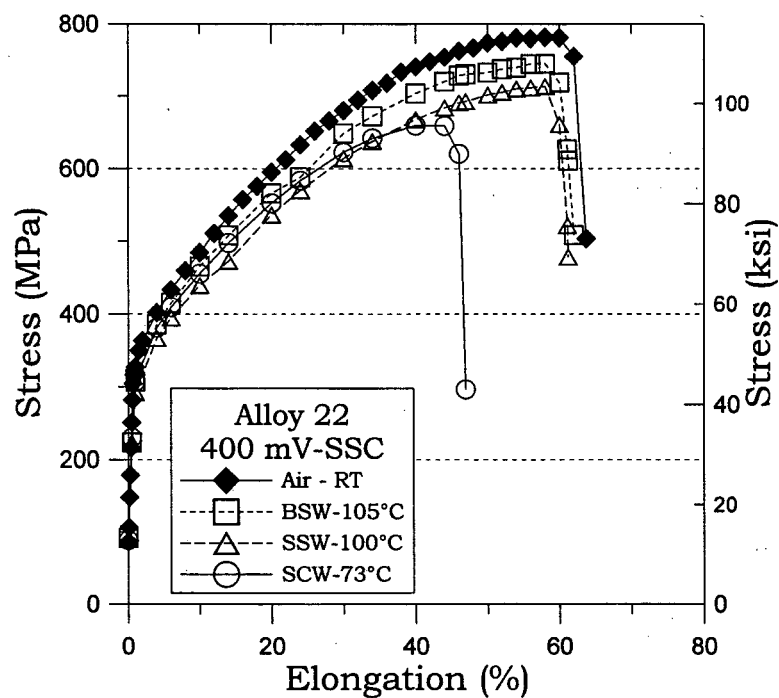


FIGURE 12: Stress-Elongation curves for Alloy 22 specimens strained at +0.4 V.

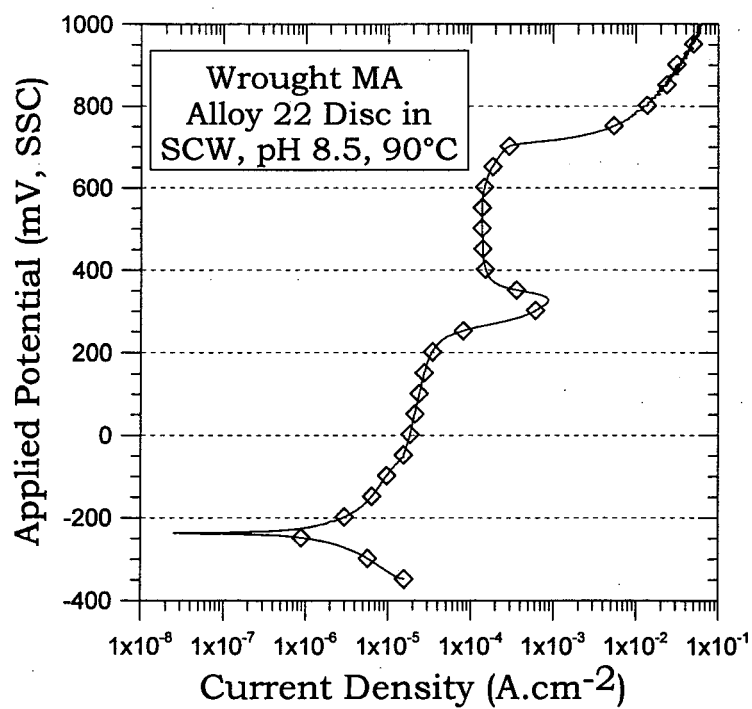


FIGURE 13: Polarization Curve for MA Alloy 22 in SCW at 90°C.

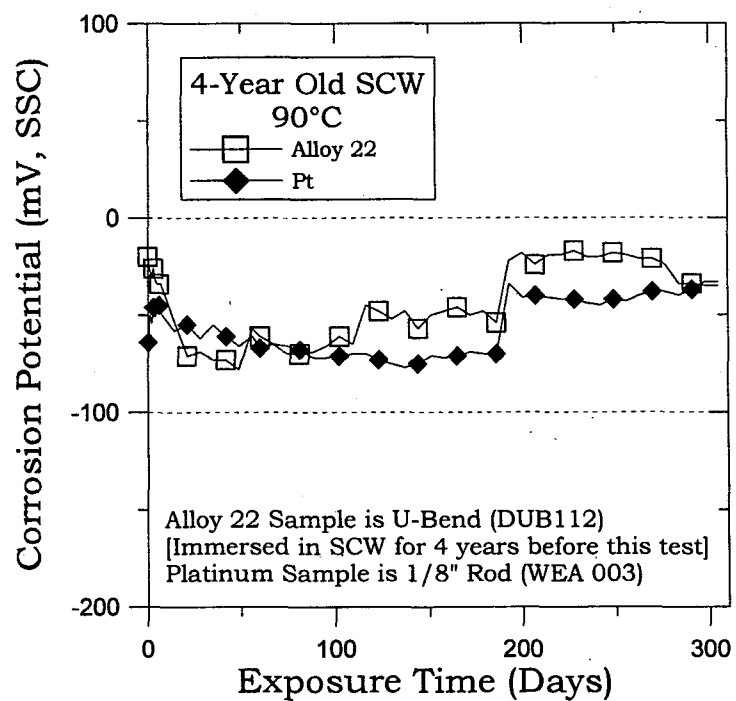


FIGURE 14: Corrosion Potential of Alloy 22 and Platinum in 4-year old SCW solution (from the Long Term Corrosion Test Facility).