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SURFACE ANALYSIS OF ALLOY 22 COUPONS EXPOSED FOR FIVE YEARS TO CONCENTRATED GROUND WATERS

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ABSTRACT

Alloy 22 (N06022) is the candidate material for the corrosion resistant, outer barrier of the nuclear waste container. Two of the potential corrosion degradation modes of the container are uniform corrosion and localized corrosion. A testing program at the Lawrence Livermore National Laboratory is being carried out for Yucca Mountain to determine the susceptibility of Alloy 22 to these two forms of corrosion using long-term immersion tests. Metallic coupons were exposed to several electrolyte solutions simulating concentrated ground water from pH 3 to 10 at 60°C and 90°C. This paper summarizes results on the characteristics of the surface deposits as well as the corrosion rate of 122 coupons of Alloy 22 obtained after more than a five-year exposure. The surface deposits consisted primarily of salt components in the respective solutions. Results showed little general corrosion and the absence of localized (crevice) corrosion.

Keywords: N06022, general corrosion, surface deposits, concentrated ground waters

INTRODUCTION

The proposed engineering barriers that will limit the release of radioactive material in the Yucca Mountain repository will consist of a sealed container and a detached drip shield. The container will be double walled with an internal barrier of type 316L stainless steel (S31603) and an external barrier of Alloy 22 (N06022). The drip shield will be made with Titanium Grade 7 (R52400). The internal barrier of the container will serve to shield radiation and also provide mechanical integrity. The primary purpose of the outer wall of the container is to provide protection against corrosion. The presence of the drip shield will guard the containers against water seepage and rock fall from the drift walls. Alloy 22 (N06022) was selected for the corrosion resistant barrier of the containers because it is well known commercially for its excellent corrosion behavior in aggressive environments. [1-5] It is nickel-based (Ni) and its nominal composition (weight percent) is ~57% nickel (Ni), 22% chromium (Cr), 13% molybdenum (Mo), 3% tungsten (W) and 3% iron (Fe). Because of its high Cr content, Alloy 22 remains passive in most industrial environments and thus, has an exceptionally low general corrosion rate.

In the absence of the drip shield, waters that contact the waste container are expected to be in the form of a multi-ionic solution. These solutions may form through two different mechanisms: (1) Dripping from the drift wall and concentrating on the container surface or (2) Deliquescence of salts that may accumulate on top of the container during dry periods. In both cases, the aqueous solution are expected to be concentrated and contain multiple component. The ground waters that are associated with the Yucca Mountain region have been well characterized. [6,7] Table 1 shows the composition of a saturated zone water (from a well designated, J-13) from near the repository site. The well water, J-13, is near-neutral and bicarbonate-rich with significant concentrations of sulfate, nitrate, chloride, alkalis and alkaline earths ions. Table 1 also shows the composition of various laboratory-prepared, aqueous, concentrated electrolyte solutions in which testing was performed. These electrolyte solutions range from pH ~3 to 10 and are designated as simulated acidified water (SAW), simulated concentrated water (SCW) and simulated dilute water (SDW). Farmer et al.[5] reported that after a 2-year immersion of Alloy 22 coupons in concentrated aqueous electrolytes from pH 2.8 to 10, at both 60°C and 90°C, the average corrosion rate by mass loss was approximately 20 nm/yr (~8 x 10^{-4} mpy). Wong et al.[8] determined the corrosion rates after a 5-year immersion in the same concentrated aqueous electrolytes to be higher for crevice coupons than weight loss coupons, but still low overall with a maximum corrosion rate of only 23 nm/yr.

The purpose of the present work was to characterize the surface of Alloy 22 coupons exposed for five years to concentrated ground waters.

EXPERIMENTAL

The corrosion rate of Alloy 22 was determined using immersion tests according to ASTM G 31 and G 1. ASTM G 31 provides guidelines on laboratory coupon immersion corrosion testing and ASTM G1 provides guidelines on coupon preparation, cleaning and evaluation. Two types of coupons were used. These were labeled (a) weight loss coupons and (b) crevice coupons. The nominal dimensions were 2 inch x 1 inch x 1/8 inch (approximately 50 mm x 25 mm x 3 mm) and 2 inch x 2 inch x 1/8 inch (50 mm x 50 mm x 3 mm), respectively. For each coupon type, there were two variants, wrought (non-welded) and welded. The coupons were fabricated from Alloy 22 plate stock and the chemical compositions for the weight loss and crevice coupons as well as the weld filler metal are shown in Table 2. All weight loss coupons were affixed with a ½" diameter PTFE or ceramic washer while all crevice coupons were affixed to the coupon holder or rack with a ¾" diameter PTFE or ceramic crevice former (CF). The purpose of the crevice former was to create an environment that might induce crevice corrosion at the contact interface, or under occluded conditions.

The electrolyte solutions used for the immersion tests were complex solutions that contained multiple ionic species. The six vessels (26 to 30) that housed the test coupons were filled with approximately 1000 liters of the specific electrolyte solution (Table 1). These series of vessels at Lawrence Livermore National Laboratory is called the Long Term Corrosion Test Facility (LTCTF). It is also important to mention that these vessels (26-30) not only contained coupons and U-bend specimens of Alloy 22 but also of other corrosion resistant alloys such as Alloy 825 (N08825), Alloy C-4 (N06455), Alloy G-3 (N06985), Alloy 625 (N06625), Titanium Grades 7, 16 and 12 (R52400, R52402 and R53400).

Each of the simulated solutions used in this study were concentrated variations of Well J-13 water (Table 1). SAW is approximately 1000 times more concentrated than J-13 and is acidified to pH ~ 3. SDW and SCW are approximately 10 and 1000 times more concentrated than J-13 water, respectively. Both SDW and SCW have a pH ~ 10. Weight loss and crevice coupons were tested at 60°C and 90°C. Approximately half of the coupons were exposed to the liquid phase of the solution (complete immersion) and the other half were exposed to the vapor phase (suspended over the liquid surface). The coupons were exposed to the testing environments at their free corrosion potential (E_{corr}). That is, external polarization was not applied to the coupons. The coupons were suspended in the test vessels from a non-metallic rack. Each coupon was electrically isolated from the other coupons. The coupons were mounted horizontally flat in the test racks. The front or label side of the coupon faced down in the vessel and the backside of the coupon faced up. The reported test temperature corresponded to the liquid phase temperature. In the testing tanks or vessels (LTCTF), the electrolyte solutions were naturally aerated, i.e. the solutions were not purged but the ingress of air above the solution was not restricted. All the tests were carried out under ambient pressure. Welded and non-welded (wrought) coupons were tested in twelve different conditions (3 electrolytes x 2 temperatures x 2 phases). The exposure time for each coupon was approximately 5 years. The actual testing time for each vessel is shown in Table 3 along with the coupon label, vessel number and average corrosion rate in nm/yr. Each coupon is designated with 3 letters and 3 characteristic numbers. The letter D represents Alloy 22 (N06022), the letter C represents crevice coupon, the letter W represents weight loss coupon, the letter A indicates that the coupon is seamless (non-welded) and the letter B indicates that the coupon does contain a weld seam. A total of 134 Alloy 22 test coupons were studied. All of the coupons were individually studied under a stereomicroscope up to 100 times magnification. Most of the coupons (122 of 134) were cleaned of surface deposits to measure the corrosion rate. Twelve welded crevice coupons, representing each of the different test conditions, were set aside for surface analyses. Energy Dispersive Spectroscopy (EDS) was performed on three coupons (DCB054, DCB114 and DCB180), immersed respectively in SAW, SCW and SDW liquid at 90°C. X-ray Photoelectron Spectroscopy (XPS) was performed on the same SAW and SCW coupons (DCB054 and DCB114). The surface analysis results and brief descriptions of the surface appearance are summarized in Table 4.

After an approximate five-year exposure to each solution/environmental condition, the coupons were removed from their respective test vessel. All 134 coupons were rinsed with de-ionized (DI) water and stored in pre-labeled, individual containers. Each coupon was then digitally photographed from the front (label side) and from the back. All coupons were then weighed three times at different times of the day to ensure complete removal of moisture. For example, coupon “X” was weighed in the morning and afternoon of Day 1 and then weighed again in the morning of Day 2. In all of the tested conditions, the coupons removed from the test vessels were covered with deposits. Therefore, the coupons were cleaned prior to final weighing for the calculation of corrosion rates by weight (mass) loss. An example of one of the weight-loss coupons is shown in Figure 1, before and after cleaning. The cleaned surface is deposit-free and illustrates the effectiveness of the cleaning solutions used. Figure 1 also shows that the coupon did not suffer noticeable corrosion in the tested electrolyte. All coupons tested in alkaline solutions (SCW and SDW) were cleaned per ASTM G 1 – C6.1, which specifies cleaning with a HCl solution at ambient temperature. The immersion time for cleaning was approximately 2 min. All coupons tested in an acidified solution (SAW) were cleaned per ASTM G 1 – C6.1 and C7.4. That is, a acid cleaning was followed by an alkaline cleaning. After the coupons were immersed in the HCl solution, they were rinsed in DI water and later immersed in hot (90-95°C) sodium hydroxide and potassium permanganate ($NaOH/KMnO_4$) for 3 min. followed by a cleaning step using a diammonium citrate ($(NH_4)_2HC_6H_5O_7$) solution at ambient temperature for 2 min. In an attempt to characterize some of the possible soluble corrosion products, aliquots of the solutions used for cleaning were analyzed using ICP-MS (Inductively Coupled Plasma Mass Spectroscopy) and ICP-AES (Inductively Coupled Plasma – Atomic Emission Spectroscopy) techniques. The solution analysis results are also shown in Table 4.

The corrosion rates of the cleaned coupons were then calculated using Equation 1,

$$CR\ (nm/yr) = \frac{8.76 \times 10^{10} \cdot \Delta W}{\rho \cdot A \cdot t} \qquad (1)$$

where 8.76×10^{10} is the proportionality constant, ΔW is the mass loss in grams after 5+ years, ρ is the density of Alloy 22 (8.69 g/cm^3), A is the exposed surface area of each coupon (cm^2) and t is the exposure time (hours).

RESULTS AND DISCUSSION

Deposits on the Immersed Coupons

As stated above, after removal from the test vessels, all coupons were covered with a varied degree of deposits (Table 4). In general, these deposits gave the coupons a characteristic appearance that varied from vessel to vessel. For example, the coupons exposed to the SAW solution were golden/brown on the label side (facing down in the vessel) and bluish/green on the backside (facing up). On the other hand, the coupons exposed to the SCW solution were gray in appearance and had a thick layer of white, salt-like deposits on the backside (facing up) (Table 4). Table 5 shows the amount of accumulated deposits in each tested condition. That is, the data in Table 5 shows the weight of the dry coupons after removal from the vessels minus the weight of the coupons before immersion in the vessels in 1997. In the vapor phase, more deposits formed at 60°C than at 90°C, and at each testing temperature, more deposits generally formed at the liquid than at the vapor phase. In a few cases, the coupons experienced weight loss even before cleaning. Table 5 shows that coupons immersed in SCW liquid at 90°C exhibited approximately 10 times the weight gain than those coupons immersed in SAW at the same temperature. This is due to the large amount of white deposits in SCW described in Table 4. The white deposit was mostly calcium carbonate ($CaCO_3$).

Table 4 briefly describes the surface appearance of the coupons from each vessel. The coupons were mostly dull, light blue-gray or tan; however, those immersed in the SAW exhibited blue and iridescent green backsides. This discoloration appears to be dependent on the vessel or solution chemistry. Other predominant features observed include rust-like deposits, mostly in the label region, white salt-like deposits scattered throughout the coupon surface and generally, a clearer crevice former (CF) annuli. That is, a lesser amount of deposits formed under the crevice former than on the surface exposed to the bulk of the solution. Similarly, the crevice former annulus of each coupon was shinier metallic in appearance than the surface exposed boldly to the solution. That is, the metal under the crevice formed seemed to have interacted less with the environment than the rest of the coupon.

Figure 2 shows some of the rust-like deposits residing in the label lettering or grooves. EDS analyses confirm high amounts of iron and oxygen (iron-oxide or rust) in the deposits at the label location. It is likely that this iron was transferred to the coupon by the labeling tool (stamp) or letter indenter. Iron oxides (hydroxides) were observed in the label regions in coupons exposed to all the vessels. However, in the acidic solutions (SAW in vessels 25 and 26), iron seemed to have dissolved more in the electrolyte and later deposited throughout all the coupons in the vessels giving them the characteristic golden color (Table 4). On the other hand, the iron present in the grooves of the label of the coupons exposed to vessels 27 to 30 (alkaline SCW and SDW) was more insoluble, that is, it stayed localized in the grooves and did not spread as much over the entire surface of the coupons in these vessels. Therefore, the coupons in the alkaline solution vessels had shades of gray (Table 4). Figure 3 shows SEM images of some of the other deposits that were observed on the coupons immersed in (a) SAW at 90°C and (b) SCW at 90°C. A summary of the deposits, as detected by EDS and XPS, is shown in Table 4. There is generally good agreement between the two analytical methods. Table 4 shows that iron is present on the entire surface of the coupons exposed to SAW; however is not present in the bold surface of the coupons exposed to SCW. EDS and XPS also detected the presence of silicon (Si), aluminum (Al) and magnesium (Mg) in the coupons exposed to SCW (Table 4). Si could have co-precipitated from the electrolyte (Table 1); however, the presence of Mg and Al in the coupons exposed to SCW cannot be fully explained. They could have been transferred with iron by the labeling tool. The deposits on the coupons exposed to SCW also contained fluoride, probably as calcium fluoride (CaF_2), which is a rather insoluble compound. The chemical analysis of aliquots of the solutions used for cleaning showed the presence of cations (such as Ca) that were part of the test solution, confirming that the deposits formed by precipitation of salts from the testing electrolytes.

Using ICP-MS and ICP-AES techniques, only silicon (Si), calcium (Ca) and magnesium (Mg) were detected in significant or reliable quantities. Si was observed in the NaOH/$KMnO_4$ solutions used to clean the coupons tested in SAW. This was expected since SiO_2 may have precipitated on the coupons in the acidic SAW and later was removed by cleaning in the caustic solution. Table 4 shows that both EDS and XPS analyses detected high concentrations of Si and O in the deposits found in Vessel 26 (SAW, 90°C). It was surprising to detect a small amount of SiO_2 in the dilute HCl solution used for the first cleaning of the coupons tested in 90°C liquid SCW since SiO_2 is not soluble in acidic solutions. Silica (SiO_2) is not expected to precipitate from an equilibrated SCW solution. High concentrations of Ca were found in all HCl solutions that were used to clean the coupons tested in SDW, those immersed in 90°C SCW and in some of the HCl and diammonium citrate solutions used to clean the coupons tested in SAW. With the exception of the citrate cleaning, these calcium results were also anticipated since $CaCO_3$ is expected to precipitate on the coupons from equilibrated SDW and SCW solutions. Table 4 shows that both EDS and XPS analyses detected significant amounts of Ca, C and O in the deposits found in Vessel 28 and 30 (SDW solution). The addition of acid (e.g. HCl) to $CaCO_3$ led to the formation of calcium ions and the evolution of CO_2 gas.

Corrosion Rates

Table 3 shows the calculated, average corrosion rates for the Alloy 22 weight loss and crevice coupons exposed to the SAW, SCW and SDW solutions at 60°C and 90°C for over 5 years. The average corrosion rates and standard deviations are presented. Even though the optical appearance and amount of deposits on coupons exposed to different solutions were different, the calculated corrosion rate was similar for coupons exposed to different vessels. The lowest rates for the weight loss coupons were observed in the SDW solution (Table 3). The highest rates for the crevice coupons were observed in the SAW solution vessels and, again, the lowest rates observed in the SDW solution vessels (Table 3). In most cases, the crevice coupons exhibited corrosion rates 2-5 times higher than the weight loss coupons in the same solutions. [8] Stereomicroscopic and scanning electron microscope (SEM) observations of both weight loss and crevice coupons indicated little or no corrosion for Alloy 22. After 5 years immersion, the machining grooves remained uniform and sharp throughout each coupon (Figures 1 and 4).

Since preferential dissolution was not observed below the crevice former annuli of the Alloy 22 crevice coupons, it was previously not clearly understood why the overall corrosion rates of the crevice coupons were generally higher than the corrosion rates of the weight loss coupons. One possible explanation is shown in Figure 4, which shows the front side and backside surfaces of the crevice coupon DCB081. The front side and backside of the crevice coupons were specified to have a surface finish of RMS16 (approximately 240 grit), however the backside of the crevice coupons had a surface finish that is not characteristic of paper grinding. This unusual aspect of the surface may have contributed to the difference in corrosion rates between the weight loss and crevice coupons. By comparison, both sides of the weight loss coupons exhibit a surface roughness of RMS32 (approximately 150 grit) (Figure 1).

Figure 5 shows a schematic representation of the welded weight loss and crevice coupons. Half of the tested coupons contained a GMAW (Gas Metal Arc Weld) seam. After 5 years of immersion testing, none of the welded coupons showed any indication of preferential weld corrosion or weld etching. The weld location was never discernible in the coupons either by optical stereo or electron microscopy. It has also been previously reported that the welded coupons did not show enhanced general corrosion rate over the non-welded coupons. [8]

Finally, in all coupons, the crevice former annuli were clear and absent of any crevice corrosion. The higher corrosion rates observed for the crevice coupons are attributed to the difference in surface finish between weight loss (Figure 1) and crevice (Figure 4) coupons and not to crevice corrosion.

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CONCLUSIONS

(1) After removal from the tanks, the color of the Alloy 22 coupons from each vessel varied as a consequence of the different types of deposits formed on them. For example, salt-like white and golden crystals containing iron.

(2) EDS, XPS, ICP-MS and ICP-AES techniques showed that the surface deposits were generally compounds that can be traced to the original solution components.

(3) Alloy 22 coupons exposed to SAW, SCW and SDW solutions at 60°C and 90°C for over 5 years exhibited very low corrosion rates. The maximum measured corrosion rate was 23 nm/yr.

(4) The crevice coupons generally exhibited corrosion rates 2-5 times higher than the smaller weight loss coupons. Stereomicroscopic observations and scanning electron microscopy indicated little or no general corrosion and the absence of crevice corrosion in all the coupons. The higher corrosion rates observed for the crevice coupons appear to be due to the different surface finish and not to crevice corrosion.

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TABLE 1
CHEMICAL COMPOSITION OF THE ELECTROLYTE SOLUTIONS (mg/L)

Ion	SDW pH 10.1	SCW pH 10.3	SAW pH 2.8	J-13 Well Water pH 7.4
K^+	34	3400	3400	5.04
Na^+	409	40,900	40,900	45.8
Mg^{2+}	1	< 1	1000	2.01
Ca^{2+}	0.5	< 1	1000	13
F^-	14	1400	0	2.18
Cl^-	67	6700	24,250	7.14
NO_3^-	64	6400	23,000	8.78
SO_4^{2-}	167	16,700	38,600	18.4
HCO_3^-	947	70,000	0	128.9
SiO_2 (aq)	~ 40	~ 40	~ 40	61.1

TABLE 2
CHEMICAL COMPOSITION OF THE STUDIED ALLOY 22 HEATS (Wt%)

Element	Weight Loss/ Crevice (Heat 2277-0-3264)	Weight Loss/ Crevice (Heat 2277-5-3203)	Weld Filler Metal (Heat 2277-4-3263)	Weld Filler Metal (Heat 2277-4-3142)
C	0.004	0.002	0.002	0.003
Co	1.14	1.82	0.89	2.03
Cr	21.3	21.3	21.6	21.17
Fe	4.4	4.0	3.6	4.24
Mn	0.29	0.19	0.32	0.25
Mo	13.4	13.08	13.5	13.81
Ni	~56	~56	~56	~55
P	0.01	0.005	0.009	0.009
S	<0.002	0.008	0.003	0.005
V	0.17	0.14	0.15	0.13
W	2.9	2.93	2.9	3.01

TABLE 3: LIST OF EXAMINED COUPONS AND AVERAGE CORROSION RATES (nm/yr)

	SAW, 60°C	SAW, 90°C	SCW, 60°C	SCW, 90°C	SDW, 60°C	SDW, 90°C
Vessel	25	26	27	28	29	30
Date in	06Feb1997	21Feb1997	10Mar1997	10Apr1997	14Apr1997	05Jun1997
Date out	20May2002	21May2002	17May2002	22May2002	10May2002	22May2002
Exp. Time, days (h)	1930 (46,320 h)	1916 (45,984 h)	1895 (45,480 h)	1869 (44,856 h)	1853 (44,472 h)	1813 43,512 h)
Weight Loss – Vapor Phase	DWA019 DWA020 DWA021	DWA059 DWA060 DWA061	DWA089 DWA090 DWA091	DWA129 DWA130 DWA131	DWA147	DWA174
Welded Weight Loss - Vapor Phase	DWB019 DWB020 DWB021	DWB059 DWB060 DWB061	DWB089 DWB090 DWB091	DWB129 DWB130 DWB131	DWB147	DWB174
Avg Rate ± s	1.9 ± 1.8	1.5 ± 1.2	0.4 ± 1.2	2.1 ± 1.0	0.4 ± 0.5	1.5 ± 1.1
Weight Loss – Liquid Phase	DWA022 DWA023 DWA024	DWA062 DWA063 DWA064	DWA092 DWA093 DWA094	DWA132 DWA133 DWA134	DWA148	DWA175
Welded Weight Loss - Liquid Phase	DWB022 DWB023 DWB024	DWB062 DWB063 DWB064	DWB092 DWB093 DWB094	DWB132 DWB133 DWB134	DWB148	DWB175
Avg Rate ± s	2.8 ± 1.4	2.3 ± 1.3	3.2 ± 1.9	9.5 ± 2.4	1.1 ± 0.5	0.8 ± 1.1
Weight Loss - Waterline	DWA034 3.6	DWA039 4.3	DWA104 2.2	DWA109 0.0	DWA154 3.0	DWA167 2.3
Crevice – Vapor Phase	DCA019 DCA020 DCA021	DCA049 DCA050 DCA051	DCA079 DCA080 DCA081	DCA109 DCA110 DCA111	DCA139 DCA140 DCA141	DCA175 DCA176 DCA177*
Welded Crevice - Vapor Phase	DCB019 DCB020 DCB021(NA)	DCB049 DCB050 DCB051(NA)	DCB079 DCB080 DCB081(NA)	DCB109 DCB110 DCB111(NA)	DCB139 DCB140 DCB141(NA)	DCB175 DCB176 DCB177(NA)
Avg Rate ± s	8.7 ± 1.3	15.1 ± 2.0	4.0 ± 2.3	5.9 ± 3.5	2.8 ± 1.7	1.0 ± 0.7
Crevice - Liquid Phase	DCA022 DCA023 DCA024	DCA052 DCA053 DCA054	DCA082 DCA083 DCA084	DCA112 DCA113 DCA114	DCA142 DCA143 DCA144	DCA178 DCA179 DCA180
Welded Crevice - Liquid Phase	DCB022 DCB023 DCB024(NA)	DCB052 DCB053 DCB054(NA)	DCB082 DCB083 DCB084(NA)	DCB112 DCB113 DCB114(NA)	DCB142 DCB143 DCB144(NA)	DCB178 DCB179 DCB180(NA)
Avg Rate ± s	10.3 ± 7.0	6.1 ± 1.5	12.9 ± 4.8	8.9 ± 3.3	5.6 ± 2.3	4.1 ± 3.3

* Data (outlier) is not included in the average and standard deviation. Thus far, a statistical treatment using the Empirical Cumulative Distribution Function (ECDF) appears to show no significant effect on the results when the outlier is removed.

NA = Not available for corrosion rates. (Reserved for surface analyses.)
s = Standard Deviation

TABLE 4
STEREOMICROSCOPE OBSERVATIONS OF THE COUPONS, 2 x 2 COUPONS (WITH A CREVICE FORMER AT ITS CENTER)

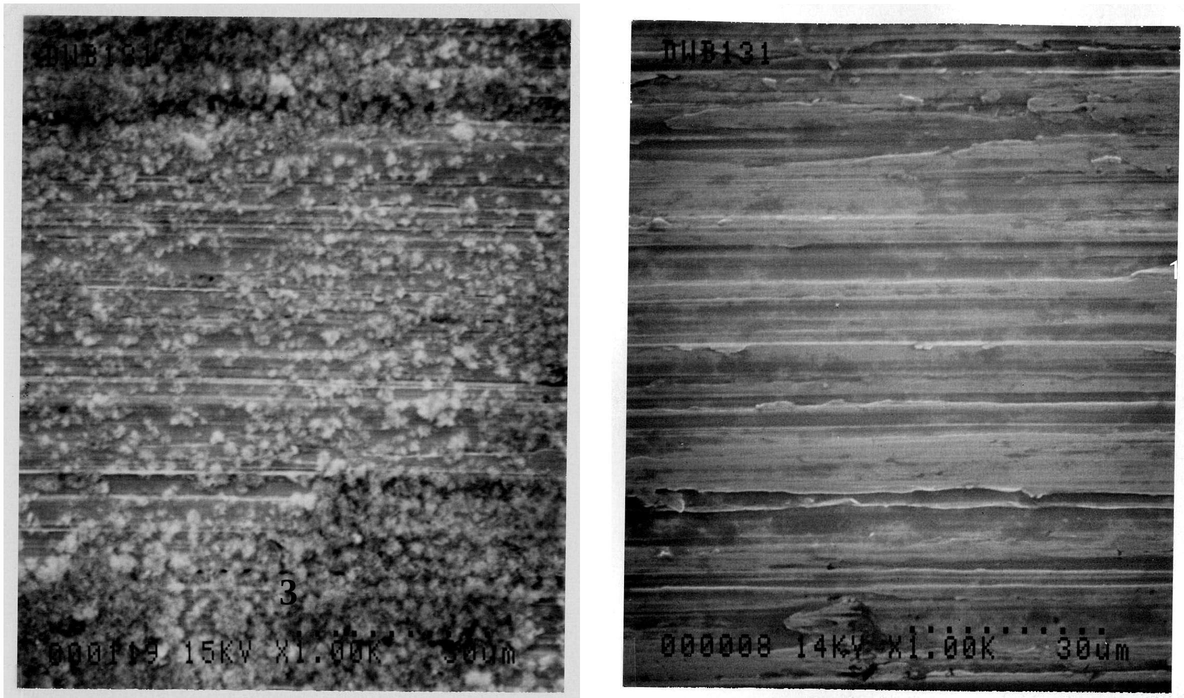
Conditions	Vapor Phase	Liquid Phase	Surface Deposits (EDS#)	Surface Deposits (XPS+)	Solution Products (ICP-MS and ICP-AES£)
Vessel 25 SAW, 60°C	Shiny, bluish-light gray with brown/rust deposits. Rust prevalent in label and edges. Few white deposits around CF*. No crevice corrosion.	Gray, blue-green and tan with rings of white and brown deposits around hole. Crevice coupons were golden/light brown with a clear, shiny CF. Few white, salt-like deposits under CF. Blue backside with dull CF. No crevice corrosion.	NA	NA	Si, Ca
Vessel 26 SAW, 90°C	Shiny, gray, spotted and highly stained. Isolated brown deposits and/or veil of tan and white deposits. Dull and dark gray CF. No crevice corrosion.	Dark, golden brown with brown deposits. Light iridescent green-golden backside. Gray CF with red edging. Abundant rust/brown deposits. No crevice corrosion.	C, O, S, K, Si, Cr, Mo, Fe, W, Ni and < 1wt.%: Na, P, Al, Cl, V, Mg, Mn, Co	C, O, Al, Si, Cr, Fe and < 1 wt.%: Na, P, F, S, Mo	Si, Ca
Vessel 27 SCW, 60°C	Bluish-purple and/or golden/yellow. Thin veil of white or tan deposits. Highly spotted crevice coupons indicate droplet condensation. Few white deposits. No weld etching or crevice corrosion.	Shiny, light gray with thin veil of gray deposits. Some white deposits around ring area. Back side is duller gray with few black and white deposits under CF. No weld etching. No crevice corrosion.	NA	NA	
Vessel 28 SCW, 90°C	Shiny, bluish-light gray, tan and yellow spotted. Thin veil of light gray or white deposits. Salts and blue ring around clear CF. Rust deposits on label. No crevice corrosion.	Dull dark gray. Thin layer of white deposits on both sides (more concentrated on backside). Shiny, clear CF on label side and light brown CF on backside. No crevice corrosion.	C, O, Si, F, Mg, Ca, Al, Ni and < 1 wt.%: Na, Ti, Cl, P, Cr, Mo, Fe, W, Co	C, O, Si, F, Mg, Ca, Al And < 1 wt.%: Na, Ti, Zn & Ni	Si, Ca, Mg
Vessel 29 SDW, 60°C	Spotted bluish-gray and tan with veil of white deposits. Some rust in label. Shiny, light gray CF. Dull, dark gray, tan and bluish backside with dull CF. Few white deposits (thin veil). No crevice corrosion.	Shiny, light tan or gray with tan and blue patches. Small veils of white deposits. Some rust in label. Shiny, light gray CF on front side and dull, dark gray CF on backside of crevice coupons. No crevice corrosion.	NA	NA	Ca
Vessel 30 SDW, 90°C	Dull with light and dark gray, tan and bluish spots and patches. Veil of white deposits. Large white deposits and transparent crystals around hole. Some rust in label. Bluish/Gray CF with rainbow ring. No crevice corrosion.	Dull, dark gray label side with abundant white deposits. Shiny, light gray/tan CF. Light gray-bluish backside. Dull, dark gray CF with rainbow ring on backside. No crevice corrosion.	C, O, Na, Si, Mg, Ca, Cr, W, Ni and < 1 wt.%: Al, S, P, Cl, Ti, Mo, Fe, Co	NA	Ca

* CF = Crevice Former (annulus)
# EDS = Energy Dispersive Spectroscopy
\+ XPS =X-ray Photoelectron Spectroscopy
£ ICP-MS = Inductively Coupled Plasma–Mass Spectroscopy; ICP-AES = Inductively Coupled Plasma–Atomic Emission Spectroscopy

TABLE 5
AVERAGE AMOUNT OF DEPOSITS (WEIGHT GAIN) ON THE TESTED ALLOY 22 COUPONS (mg) BEFORE CLEANING

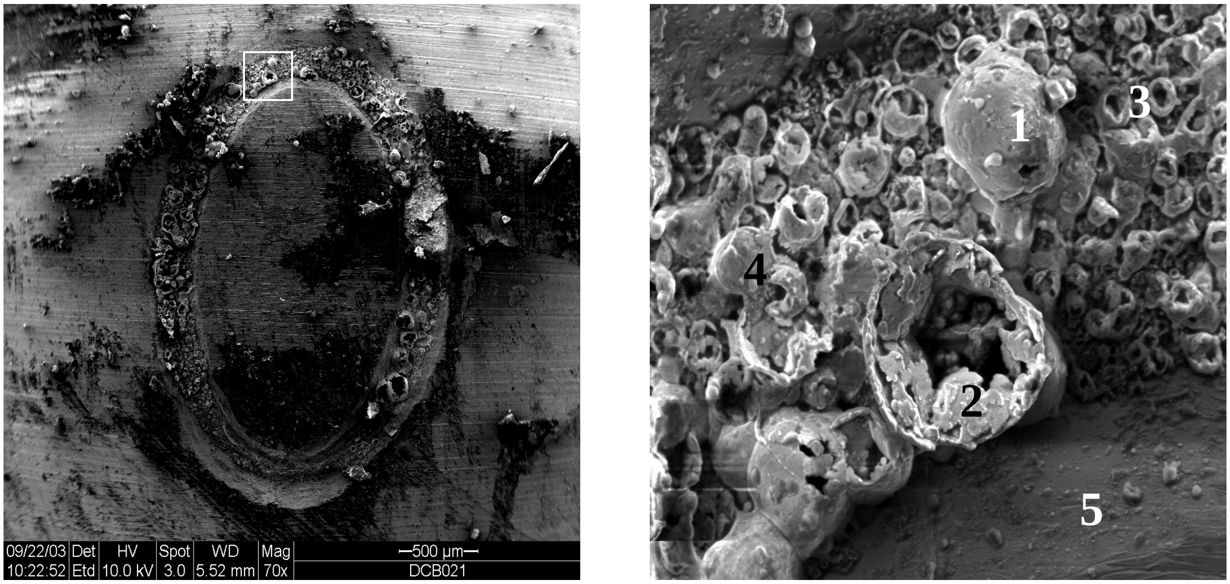
	SAW, 60°C	SAW, 90°C	SCW, 60°C	SCW, 90°C	SDW, 60°C	SDW, 90°C
Vessel	25	26	27	28	29	30
Weight Loss Coupon – Vapor Phase Welded & Nonwelded Avg Wt Gain ± s	1.1 ± 0.5	0.7 ± 0.4	1.5 ± 0.5	0.7 ± 0.4	NA	10.8 ± 4.5
Weight Loss Coupon – Liquid Phase Welded & Nonwelded Avg Wt Gain ± s	8.6 ± 3.0	5.4 ± 0.5	1.5 ± 1.3	44.7 ± 12.4	NA	10.3 ± 0.6
Weight Loss - Waterline	3.5	2.2	3.7	3.5	NA	53.7
Crevice Coupon - Vapor Phase Welded & Nonwelded Avg Wt Gain ± s	1.2 ± 0.7	-1.8 ± 0.3	0.7 ± 0.4	0.7 ± 0.6	1.0 ± 0.3	4.6 ± 5.0
Crevice Coupon - Liquid Phase Welded & Nonwelded Avg Wt Gain ± s	5.8 ± 0.5	8.2 ± 0.9	-0.4 ± 0.8	120.6 ± 5.6*	0.2 ± 0.4	25.5 ± 0.7

* Data (outlier) is not included in the average and standard deviation. There is an apparent measurement error.
NA = Not available.
s = Standard Deviation



(a) (b)

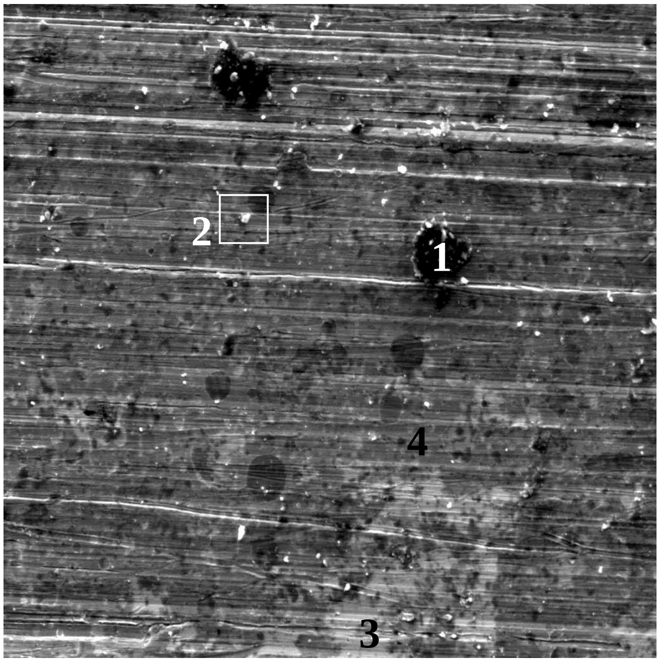
FIGURE 1. Alloy 22 weight-loss coupon, DWB131 (90°C, SCW, Vapor),
(a) before and (b) after cleaning (1000X magnification).



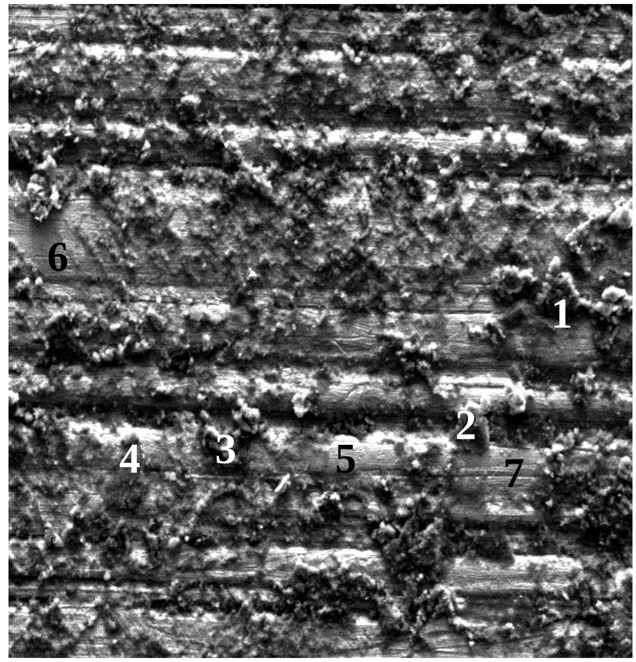
(a) (b)

Element	Deposit 1 Wt.% (1)	Deposit 2 Wt.% (2)	Deposit 3 Wt.% (3)	Deposit 4 Wt.% (4)	Base 1 Wt.% (5)	Alloy 22 (nominal) Wt.%
C	19.31	26.89	25.91	21.23	24.88	
O	33.43	35.92	32.47	32.70	11.35	
Si	0.47	0.34	0.53	0.41		
Al			0.28			
Cl	0.27	0.73	0.29	0.15		
S	0.16	1.06	0.75	0.60	1.19	
P		0.22	0.27			
Cr	0.77	0.53	1.07	0.90	12.79	22
Mo	2.48	1.99	2.76	1.05	7.04	13
Fe	40.24	30.76	33.94	40.79	9.01	3
W					3.37	3
Co	2.88	1.56	1.72	2.18	1.04	2
Ni					29.32	57

Figure 2. EDS analyses of rust-like deposits in stamped label of DCB021 (90°C, SAW, Vapor) (a) 70X magnification (b) 1000X magnification.



(a) DCB054 Bold - 90°C, Liquid, SAW (pH ~ 3)



(b) DCB114 Bold - 90°C, Liquid, SCW (pH ~ 10)

Element	Deposit 1 Wt.% (1)	Deposit 2 Wt.% (2)	Base 1 Wt.% (3)	Film Wt.% (4)	Alloy 22 Wt.%
C	58.29	10.28	5.21	9.76	
O	12.82	30.98	4.83	15.86	
Na	0.19	0.80			
Si	0.10	10.61			
Al	0.35	0.93	0.29	0.48	
S	0.61	0.71		1.97	
Mg		0.20			
P	0.36	0.34	0.47	0.53	
Cr	6.11	8.21	19.29	15.59	22
Mo	2.71	5.22	8.76	6.65	13
Fe	9.57	7.91	4.83	10.23	3
W	2.44	9.72	5.53	5.48	3
Co	0.59	0.74	1.60	0.59	2
Ni	5.87	13.34	47.68	32.86	57

Element	Deposits Wt.% (1-4)	Base Wt.% (5-7)	Alloy 22 (nominal) Wt.%
C	57-81	8-16	
O	12-22	7.7-8.2	
Na	0.3-0.8		
Si	1-5		
Al	0.3-0.8	0.4-0.5	
S		2-3	
Mg	0.5-4.0		
F	0.5-4.0		
Ca	1-4		
Cl	0.1		
S		2-3	
P	0-0.3	0-0.5	
Ti	0.4-4.0		
Cr	0.2-0.9	17-19	22
Mo	0.2-1.1	9-12	13
Fe	0.1-0.3	3.5-4.1	3
W	0-3	6.5-7.4	3
Co	0.1	1.1-1.7	2
Ni	0.4-1.4	35-39	57

Figure 3. EDS analyses of (a) DCB054 and (b) DCB114.

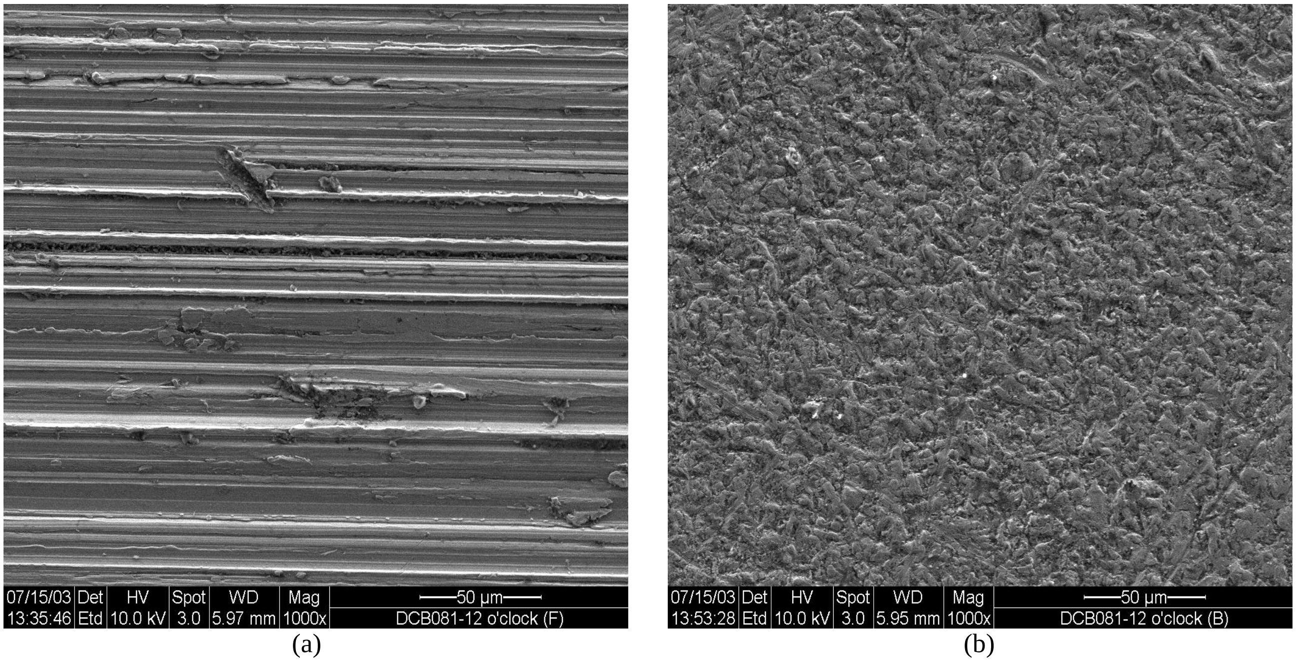


FIGURE 4: SEM images of crevice coupon, DCB081 (60°C, SCW, Vapor).
(a) the front side (b) the back side (1000X magnification).

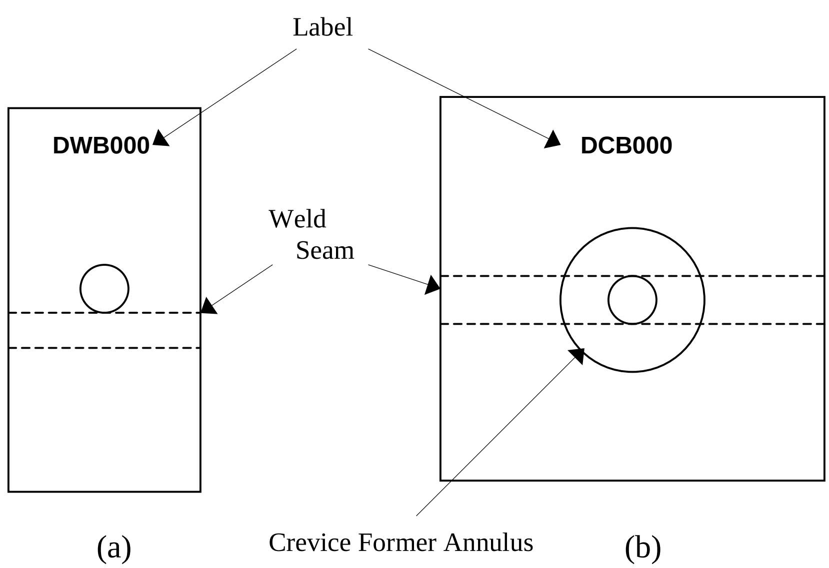


FIGURE 5 - Schematic of Welded (a) Weight Loss and (b) Crevice Coupons.