*Electrodissolution Studies of 304 Stainless
Steel in Sodium Nitrate Electrolyte*

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ELECTRODISSOLUTION STUDIES OF 304 STAINLESS STEEL IN SODIUM NITRATE ELECTROLYTE

by

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ABSTRACT

To explore the impact of a wide range of operating parameters upon 304 stainless steel (SS) dissolution in sodium nitrate (NaNO_3) electrolyte, the staff of Engineering Science Applications-Energy and Process Engineering performed a series of beaker experiments. The variables that we explored included NaNO_3 concentration, chromate concentration, pH, stirring rate, and current density. We adjusted the run length to obtain approximately 10 mg/cm^2 metal removal so that we could compare surface finishes under similar test conditions.

Key findings may be summarized as follows. Current efficiency during dissolution depends most strongly upon current density and electrolyte concentration. At 0.05 A/cm^2 , current density is more dependent upon chromium concentration than we previously thought. We obtained the best surface finish in a classical electropolishing regime at current densities above 1.5 A/cm^2 . Mirror-like finishes were obtained at near 100% current efficiency.

At 0.05 A/cm^2 we obtained reasonable surface finishes, particularly at lower electrolyte concentration. Current efficiency was low (30%). At intermediate current densities (0.3 A/cm^2), we obtained the worst surface finishes, that is, surfaces with severe pitting.

Also, we explored preferential attack of the weld zone during electrodisolution of 304 stainless steel cans. Cans were processed with the weld zone shielded and unshielded. Electrodisolution removed approximately twice as much material from cans with unshielded weld zones as from cans with shielded weld zones. Because welds cover

approximately 6% of the can area, the depth of metal removal from the welds is 15 times greater than from the remainder of the can.

The following implications are apparent. While operation above 1 A/cm^2 yields the best surface finish at 100% current efficiency, equipment size and power feedthrough limitations reduce the attractiveness of this option. The next-best surface finish is obtained at low current densities (0.05 A/cm^2); however, preferential attack of weld zones occurs. Because other Los Alamos researchers, Wedman et al., obtained more favorable results with the sulfate electrolyte, we recommend no further work for the sodium nitrate electrolyte system and that research efforts be concentrated on the sulfate electrolyte system.

INTRODUCTION

In support of the Los Alamos National Laboratory (LANL) Plutonium Facility, the staff of Engineering Science Applications-Energy and Process Engineering is developing electrolysis to decontaminate metal surfaces. Cans and gloveboxes made of 304 stainless steel (SS) are cleaned with neutral electrolytes. In this process, dissolved metals precipitate as hydroxides that aid in flocculating actinides removed from the surface during decontamination. A previous effort to decontaminate SS at LANL was described by Wedman et al.¹

We performed a series of experiments to determine the effect of operating conditions upon current efficiency of metal dissolution with sodium nitrate electrolyte. We explored the conditions of current density, chromium content of the electrolyte, NaNO_3 concentration, initial pH, and stirring rate. Also, by varying dissolution times, we were able to investigate the quality of surface finish at similar levels of total metal removal.

In addition, we explored the relative dissolution rate on weld zones. To quantify the effect of enhanced mass removal, we conducted tests with the weld zone both shielded and unshielded. Our attention was focused on total mass removal, current density, and preferential mass dissolution. Significantly more mass removal was observed on the rim of the cans at the two places where the end caps are welded to the cylindrical component than over the remainder of the can surface.

EXPERIMENTAL APPARATUS AND PROCEDURES

Tests were performed with 304 SS rods with three slightly different compositions. Test series from these specimens are designated as SA, SB, and SC.

To perform beaker tests, we used an AFCBP1™ bipotentiostat made by Pine Instruments. The working electrodes were constructed by two methods. For series SA tests, we potted a 1/8-in. 304 SS rod in epoxy. We found that the surface area of the end of the rod was insufficient to obtain accurate weight-loss measures. Subsequently, in series SB and SC we mounted 1/4-in. 304 SS rods in a tightly sealed Teflon™ tube, as shown in Fig. 1.

Fig. 1. Schematic of electrode and TEFLON™ holder used in SB and SC series tests.

Other cell components consisted of a counter electrode, reference electrode, and pH electrode. Bath temperature was also measured. A counter electrode consisted of a 1-in.-square platinum flag with platinum wire extension. A double-junction calomel reference electrode aided in essentially eliminating contamination of electrolytes with chloride ions.

We polished the electrode surface wet on an 8-in. wheel. The electrodes were held during polishing in a specially made 304 SS tube filled with epoxy and with a 1/4-in. hole through the middle that held the electrode perpendicular to the polishing surface. After an initial coarse grinding step with a 240-grit abrasive disk, we used abrasive disks with grits of 400, 600, and 800, culminating with the use of 1200-grit disk that yielded a reflective surface.

Next, the sample was weighed and mounted in the TEFLON™ holder. We filled a 250-ml beaker with 100-ml of electrolyte. Then we placed the electrode assembly 0.5 in. away from a 1-in.-long stirring rod. Next, we placed the counter electrode and pH probe on the side of the beaker. The tip of the reference electrode was placed as close to the working electrode as possible. We monitored the rotation rate of the stirring bar. For instance, at a setting of 2 we obtained a rotation rate of 80 rpm. As the stirrer warmed up, we readjusted the rate to 80 rpm. By varying the stirring rate and observing the surface finish, we found that the solution agitation was an important variable in the electropolishing regime.

Mill specifications for electrodes used in series SB and SC tests are given in Tables I and II. Sample SC appears to be significantly harder. It contains a higher carbon content, tensile strength, yield stress, and lower elongation at failure.

Table I. Chemical Composition of 304 SS Samples (expressed as percent)

Sample	C	Si	Mn	P	S	Ni	Cr	Mo	Cu	N	Co
SB	0.042	0.45	1.28	0.031	0.015	9.53	18.18	0.24	0.51	0.029	—
SC	0.07	0.31	1.14	0.07	0.020	8.62	18.16	0.26	0.43	0.048	0.16

Table II. Mechanical Properties of 304 SS Samples

Sample	Tensile Strength (kpsi)	Yield Strength (kpsi)	Elongation at Failure (%)	Reduction in Area (%)	Hardness, Brinell Number (kg/m ²)
SB	104	52	46	77	199
SC	119	109	36	64	—

Weld Zone Electrodeposition

The relative dissolution rate of weld zones compared with the dissolution rate for the remainder of the can was obtained by first testing a can at a given voltage and measuring the weight loss. We then covered the welds with epoxy and reran the test at the same potential and time. Differences in dissolution indicated losses from the weld zone.

We constructed the cans by fusion welding end caps onto a 4.4-in. diameter by 9.3-in.-long 304 SS tube. We conducted the tests with a solution of sodium nitrate at a concentration of 260 g/L, a total current of 40 A, and for a 30-min-per-test run. Test parameters are summarized in Table III.

Table III. Test Parameters Used During Mass Dissolution from Cans

Cans:	
Material	304-L SS
Diameter	4.4 in.
Length	9.3 in.
Surface Area	1 037 cm ²
Fabrication Method	Fusion weld
Electrolyte Solution:	
Electrolyte	Sodium nitrate (NaNO ₃)
Concentration	260 g/L
Circulation	Average velocity of 5 cm/s along can surface
Test Conditions:	
Total Current	40 A
Current Density	39 mA/cm ²
Average Voltage	3.8 V
pH Range	10.2–11.4
Test Duration	30 min
Temperature Range	20–40°C

We placed the cans in a fixture that allows the electrolyte to circulate in a closed loop. A more comprehensive description of the fixture set-up and the results of previous tests is given by Martinez.² The fixture forms a concentric cylinder with the can. Insulating spacers are used to maintain a constant gap between the can and the fixture. Current is applied to the can through electrical conductors on both end caps. The can acts as the anode and the fixture acts as the cathode. Solution is introduced at the fixture's lower end cap, flows along the can surface, then leaves the fixture through the end cap on the opposite end. The flow path of the solution is from a reservoir to a centrifugal pump, to the decontamination fixture, and back to the reservoir. The reservoir is open to the atmosphere to allow purging of gases produced during electrolysis.

The procedure for each test run was as follows:

- measure mass of cans,
- place can in fixture,
- establish solution circulation,
- apply current to 40 A,
- monitor current, voltage, solution temperature, and pH,
- run test for 30 min,
- shut off power,
- remove can from fixture,
- rinse, then dry can, and
- measure mass of can.

The following parameters remained constant in the tests we ran: current density, test duration, flow velocity, and solution concentration. After each run we recorded mass removal.

CHEMISTRY AND CALCULATIONS

During electrodisolution of 304 SS, decontamination occurs at the anode. Competing anodic reactions are oxygen evolution and reoxidation of chromium that had been reduced at the cathode. Hydrogen evolution is the primary reaction at the cathode. Side reactions include chromium reduction and nitrate reduction. Reactions are given below.

If the pH is greater than 6.5, chromate ions are the predominate hexavalent chromium species present.

At the anode the following reactions occur:

with side reactions

At the cathode, the main reaction is:

with side reactions

Although we generally used an alkaline electrolyte, for simplicity the reactions above are given with hydrogen ions. Review of the oxidation reactions indicates that dissolution of iron and nickel is pH neutral. (This conclusion is obtained, for instance, by adding 2 of reaction [1(a)] to 3 of reaction [3] so that electrons produced are equal to electrons consumed.) Chromium dissolution, however, is a net producer of H^+ that would make the solution more acidic with time. The decrease in pH with time is apparent in the experimental results given in Tables IV(a), (b), and (c).

Side reactions at the cathode can make the electrolytes more alkaline. This is particularly true for reaction 4(b), as pointed out by John Huang.³ When the cathode is the same size as the anode, reaction 4(b) dominates over reaction 1(c) and the solution becomes more alkaline in nitrate solutions. Since the cathode area is 40 times greater than the anode, reaction 1(c) dominates pH changes in the beaker experiments.

Current efficiency at the anode may be defined as the ratio of current that oxidizes the electrode [reactions 1(a-c)] to the total current passed by reactions 1(a-c) and reactions 2(a,b). Based upon alloy composition and dissolution of Fe, Ni, and Cr to the +3, +2, and +6 valence states, 6 106 ampere-seconds (coulombs) are equivalent to 1 g of 304 SS. If 16 000 ampere-seconds are passed to dissolve 1 g of alloy, the current efficiency is 0.38 or 38%. Thus, 62% of the current is used to produce oxygen and oxidize Cr^{+3} if present.

Once the current efficiency is known for a set of conditions, total mass removal may be calculated as:

$$\dot{M} \left(\frac{\text{mg}}{\text{cm}^2} \right) = 9.83 \frac{\eta \text{ I(A) } t(\text{min})}{S(\text{cm}^2)} \quad [5]$$

where η is the current efficiency and S is the electrode surface area.

Table IV(a). Series SA Electrodissolution Results

SA diameter (in.) = 0.125

SA surface area (cm²) = 0.07913

Cr content of 304 SS = 0.181

Date 4/16/96

Electrode	NaNO ₃ g/L	Calc Start Cr ⁺⁶ g/L	Current Density A/cm ²	Stirrer Setting	pH Initial	pH Final	Time min	Time s	Time total	Wt Initial	Wt Final	Temp °C	Voltage Initial	Voltage Final	Weight Removed mg/cm ²	Current Efficiency %
SA1	600	0	0.045	3	10.25	10.13	53	56	53.93	9.0658	9.0648	28.7	1.75		12.64	53.0
SA2	600	0.00181	0.5	3	10.12	10	3	40	3.667	9.9573	9.9562	29.4	1.9		13.90	77.2
SA3	600	0.0038	5	3	9.96	9.88	0	10	0.167	9.4668	9.4655	29.6			16.43	200.6
SA4	600	0	0.045	3	10.11	10.05	50	0	50	9.5803	9.5794	27.2	1.79	1.76	11.37	51.4
SA5	600	0.00163	0.5	3	10.03	9.87	3	22	3.367	9.6578	9.6567	27.9	1.88		13.90	84.0
SA6	600	0.00362	5	3	10.04	9.98	0	13	0.217	9.3107	9.3099	28.2	4.04		10.11	95.0
SA7	600	0.00507	5	2	9.96	9.83	0	13	0.217	8.0482	8.0472	24.3	6		12.64	118.7
SA10	600	0.00688	0.5	2	10.1	9.99	3	30	3.5	7.8668	7.8655	24.5	1.87		16.43	95.5
SA1	600	0.00923	0.1	2	10.12	10.07	13	0	13	9.0289	9.028	25	1.94		11.37	89.0
SA2	600	0.01086	0.05	2	10.03	9.97	50	0	50	9.9132	9.9127	25.2	1.85	1.81	6.32	25.7
SA2	600	0.01176	0.05	2	10.02		50	43	50.72	9.9127	9.9111	26.6	1.85		20.22	81.1
SA3	600	0.01466	1	0	9.98		1	5	1.083	9.4249	9.424	27.5	2.08-3.8	2.3	11.37	106.8
SA9	600	0.01629	1	2	10	27.4	1	5	1.083	9.2644	9.2634		2.1-3	2.34	12.64	118.7
SA8	600	0.0181	2	2	10.03		0	32	0.533	9.3889	9.3878	27.7	6.07	3.3	13.90	132.6

Table IV(b). Series SB Electrodisolution Results

SB diameter (in.) = 0.25

SB surface area (cm²) = 0.316

Cr content of 304 SS = 0.182

Date 5/21/96

Electrode	NaNO ₃ g/L	Calc Start Cr ⁺⁶ g/L	Current Density A/cm ²	Stirrer Setting	pH Initial	pH Final	Time min	Time s	Time total	Wt Initial	Wt Final	Temp °C	Voltage Initial	Voltage Final	Weight Removed mg/cm ²	Current Efficiency %
SB1	600	0	1	2	8.8	7.23	1	0	1	23.9477	23.9446	25.8	3		9.79	99.7
SB2	600	0.01164	3.096	2	7.07	6.49	0	31	0.517	25.2091	25.204	26.5	8	5	16.11	102.5
SB3	600	0.02309	0.3	3	6.8	6.53	4	67	5.117	25.1075	25.1045	26.9	1.99		9.48	62.8
SB4	600	0.02636	0.3	2	6.59	6.19	3	25	3.417	25.1892	25.1861	27.2	1.96		9.79	97.2
SB5	600	0.00564	0.05	2	7.49	7.04	50	0	50	24.0062	24.003	25.2	1.64		10.11	41.2
SB6	600	2	1	2	7	6.97	1		1	23.4939	23.4908	27.1	2.82		9.79	99.7
SB7	600	2	0.05	2	7	7.14	50	0	50	23.7095	23.7066	27.5	1.66	1.7	9.16	37.3
SB8	600	2	0.3	2	7.03	7.15	3	23	3.383	23.4544	23.4515	28.2	1.95	2	9.16	91.9
SB9	600	2	3.096	2	7.13	7.11	0	19	0.317	23.334	23.3312	28.3		5	8.85	91.8
SB10	600	2	0.05	2	10.97	10.97	53	16	53.27	23.6971	23.6933	22.5	1.73		12.01	45.9
SB11	600	2	0.3	2	10.91		3	27	3.45	21.7924	21.7891	22.8	2.01		10.43	102.5
SB12	600	2	3.096	2	10.93		0	20	0.333	23.6445	23.6412	23.3	8	4	10.43	102.8
SB13	600	12.5	3.096	2	7.02		0	19	0.317	23.7094	23.7062	24.5	8	5	10.11	104.9
SB14	600	12.5	0.3	2	7.01		3	24	3.4	23.6098	23.607	24.6	2.02		8.85	88.3
SB15	600	12.5	0.05	2	7	6.99	156	58	157	23.6644	23.6603	24	1.7		12.95	16.8
SB1	600	12.5	0.05	2	10.92	10.89	241	0	241	23.902	23.8986	24.7	1.68		10.74	9.1
SB16	600	12.5	0.3	2	10.7		3	40	3.667	23.4679	23.4646	25.1	2.06		10.43	96.5

Table IV(c). Series SC Electrodisolution Results

SC diameter (in.) = 0.25

SC surface area (cm²) = 0.316

Cr content of 304 SS = 0.182

Date 6/13/96

Electrode	NaNO ₃ g/L	Starting Cr ⁺⁶ g/L	Current Density A/cm ²	Stirrer Setting	pH Initial	pH Final	Time min	Time s	Time total	Wt Initial	Wt Final	Temp °C	Voltage Initial	Voltage Final	Weight Removed mg/cm ²	Current Efficiency %
																SC Series
SC1	200	0	0.3	2	8.7	8.15	3	56	3.933	22.7509	22.7489	23	2.44		6.32	54.5
SC2	200	0.0069	0.3	2	7.4	6.18	12	0	12	22.9047	22.9016	23.5	2.8		9.79	27.7
SC3	200	0.01253	0.05	2	6.9	6.34	53.02	0	53.02	22.7361	22.7335	24.6	1.74	1.9	8.21	31.5
SC4	200	0.01725	3.096	2	7.2	6.9	0	20	0.333	22.8937	22.8906	25.6	6.6		9.79	96.6
SC5	200	0.02288	3.096	0	6.9	6.3	0	19	0.317	22.8132	22.81	26.2	6		10.11	104.9
SC6	200	0.02869	3.096	2	10.44	10.12	0	20	0.333	23.525	23.5217	26.3	6.6		10.43	102.8
SC7	200	0.03505	0.3	2	10.32	10.18	12	0	12	22.7016	22.6988	26.6	2.3	2.6	8.85	25.0
SC8	200	0.0365	0.05	2	10	9.68	64	33	64.55	22.6403	22.6379	26.9	1.72		7.58	23.9
SC9	34	0	0.3	2	10	9.28	54	69	55.15	22.7512	22.7481	26	4		9.79	6.0
SC10	34	0.00563	1.26	2	10.1	9.5	4	57	4.95	22.6403	22.6379	27.5	1.72		7.58	12.4
SC11	34	0.00999	0.05	2	10.2	9.44	232	106	233.8	22.6403	22.6379	27.5	1.72		7.58	6.6

RESULTS

The conditions that we explored were current density, chromium content of the electrolyte, NaNO_3 concentration, initial pH, and stirring rate. Tables IV(a), (b), and (c) give operating conditions, total metal weight loss, and calculated current efficiency. Microscopic observations are also described.

Current Efficiency for Dissolution

Review of Tables IV(a), (b), and (c) indicates that current efficiency is most dependent upon current density and sodium nitrate concentration. As the current density increases, the current efficiency rises to 100% at high electrolyte concentration (Fig. 2).

Values greater than 100% reflect the $\pm 5\%$ error in weight measurements that were input to current efficiency calculations. Because the current efficiency calculation assumes a solution valence state for each metal species, dissolution to a lower valence state can also yield current efficiencies greater than 100%. No oxygen evolution is observed at 100% current efficiency. At greater than 1 A/cm^2 , electropolishing becomes apparent at the edge of the electrode where the local current density is highest.

We also observed that the current efficiency is lower for lower electrolyte concentrations. At 34 g/L , which corresponds to 0.4 M , the current efficiency is about 10%. This is approximately the same ionic strength as the $0.2 \text{ M Na}_2\text{SO}_4$ solution that we are currently exploring.

Early work by Hoare and others on the properties of passive films helps to explain a lower current efficiency at lower ionic strength.⁴ A good protective film is an electronic conductor that allows passage of current only by oxidizing water to oxygen gas. The ion-replacement model suggests that when the oxide matrix is attacked by anions, it exhibits ionic conductivity that results in metal dissolution; thinning of the oxide layer was also reported.⁵ Thus, higher current densities associated with higher field gradients across the passive layer will increase anion penetration and dissolution. Higher anion concentrations will also increase the rate of attack and thus the current efficiency for metal dissolution.

Fig. 2. Impact of current density upon current efficiency for dissolution of 304 SS, pH = 7 and 10, NaNO₃ concentration 200 and 600 g/L.

We explored the effect of chromium content of the electrolyte upon current efficiency (Fig 3). Earlier work by Childs and Winkel showed a decrease in current efficiency with increased chromium content of the electrolyte.⁶ We were interested in confirming trends for our concentration range and current densities. Therefore, we explored chromium concentrations up to 12.5 g/L. These concentrations correspond to cleaning 10 cans with a system electrolyte volume of 4.5 L.

At 0.05 A/cm², the current efficiency dropped by more than 50%. At high current densities, we saw little change in current efficiency with concentration. Results at higher current density agree with those of Childs and Winkel.⁶ Because Cr(OH)₃ is insoluble in alkaline solutions, chromium oxidation back to the Cr⁺⁶ at the anode may not be responsible for the loss in current efficiency. Instead, formation of a chrome-rich oxide layer that improves electronic conductivity of the oxide layer, may enhance oxygen evolution. Because a low current density is all that is currently obtainable in the can decontamination work, greater attention needs to be paid to the chromium content of the electrolyte than we had previously thought.

Fig. 3. Impact of chromium concentration upon current efficiency, NaNO_3 concentration is 600 g/L.

In order to derive a correlation and determine the level of significance for each parameter, we applied a stepwise multivariable regression to the current density results. The best correlation was as follows:

$$\text{CE} = -0.568 + 0.403 \log(i) + 0.567 \log(C_{\text{NaNO}_3}) \quad [6]$$

where the goodness of fit is described by Tables V(a) and (b) below.

Tables V(a) and (b). Statistical Significance of the Correlation Between Current Efficiency and Independent Variables

Source	Sum of Squares	Differential	Mean Square	F-ratio
Regression	5.23682	2	2.61841	53.9
Residual	1.89603	39	0.048616	

Variable	Coefficient	Standard Error of Coefficient	T-ratio	Probability
Constant	-0.567843	0.2570	-2.21	0.0331
Log "i"	0.402977	0.0481	8.37	≤0.0001
Log(NaNO ₃)	0.566509	0.0975	5.81	≤0.0001

Predicted efficiencies in contrast to the actual current efficiencies are plotted in Fig. 4. The scatter in the fit indicates the error in weight measurements that was especially apparent in data from series SA. Chromium concentration and pH were initially included in the correlation but they did not improve the fit significantly. For instance, when chromium concentration was added, the F-ratio actually went down; indicating that the better fit did not justify including the additional parameter.

Wedman et al. also found that higher current densities and electrolyte concentrations increase current efficiency.¹ Because Wedman et al. explored a wider pH range, they observed higher current efficiencies in acidic solutions. In contrast, because we investigated a narrower pH range, we saw little effect.

SURFACE PROPERTIES

We took surface micrographs of each electrode at 200 times magnification and ran samples for sufficient time so that a similar average metal removal was obtained for each sample. Thus, micrographs have a common basis. Because current densities are higher at the edge of the samples than in the middle, two pictures were taken for each specimen.

In order to quantify the variation in current density across the electrode surface, Newman solved the applicable set of equations for the current distribution across a rotating disk electrode.⁷ The electrode configuration applied in this study has the same geometry as a rotating electrode. If the current distribution is determined only by solution resistance, the current density at the center of the circle is half the average and approaches infinity at the edge. Both kinetic resistance and mass-transfer limitations create a more uniform current distribution.

Fig. 4. Goodness of fit comparison between predicted and actual current efficiencies.

The applicable dimensionless group for describing the transition from ohmic control toward a uniform current distribution caused by kinetic resistance is

$$J = (\alpha_a + \alpha_c) \frac{i_o F r_o}{RT \kappa} \quad [7]$$

where

- a = charge transfer coefficients,
- i_o = exchange current density, A/cm²,
- r_o = electrode radius, cm,
- κ = solution conductivity, S/cm,
- F = Faraday constant (96 500 C/g-equiv),
- R = ideal gas constant, and
- T = temperature, K.

As J becomes larger, the current distribution becomes more nonuniform. For the following discussion, greater current density variations are expected for more reversible surface reactions on larger electrodes in more dilute electrolytes. At this time, measurements of a and i_0 are not available to evaluate Eq. 7.

Surface observations are discussed below at three current densities: 0.05, 0.3, and 3.1 A/cm². Generally, these three levels summarize the full range of behavior that we observed.

Current Density of 0.05 A/cm²

Etching characteristics at 0.05 A/cm² are summarized in Fig. 5. For 200 g/L NaNO₃, Fig. 5(a) illustrates surface etching where the grain structure is apparent as regions with parallel lines or steps. Relatively few pits are apparent. When electrolyte concentration is increased to 600 g/L, the current efficiency rises from 30% to 50%. Surface pitting, however, becomes more predominant [Fig. 5(b)].

Effects of other changes in electrolyte composition may also be explored. Comparison of Figs. 5(b) and (c) shows that a pH change from 7 to 10 causes little change in surface character. Increasing the chromium concentration from essentially zero to 12.5 g/L decreases the current efficiency but improves surface properties, as shown in Fig. 5(d).

Current Density of 0.3 A/cm²

When the average current density increases to 0.3 A/cm², pitting increases markedly. In addition, surface etching appears to decrease because surface scratches from polishing become more apparent [Fig. 6(a)]. As stirring decreases, pitting becomes widespread [Fig. 6(b)]. As the electrolyte concentration decreases from 600 to 200 g/L, surface etching is enhanced [Fig. 6(c)], but at the expense of lower current efficiency (30% compared with 100%). Finally, a pH change from 7 to 10 appears to have little effect upon surface appearance [Fig. 6(d)].

Current Density of 3.1 A/cm²

At high current densities, a classical electropolishing regime is attained. Datta and Landolt also found that electropolishing in nitrate solutions required high current densities.⁸ It is generally accepted that classical electropolishing develops when a salt film is formed on the electrode surface. Salt film occurs at lower current densities in phosphate electrolytes with low solubility of iron phosphate. Lower mass transport and lower temperatures also tend to encourage salt film formation.

Characteristics of electropolishing are seen in Fig. 7(a). A mirror-like finish is produced. Under some conditions, preferential dissolution at grain boundaries is apparent, along with the formation of shallow hemispherical pits [Fig. 7(b)]. Electropolishing is also characterized by a current efficiency of unity.

At 3 A/cm^2 variations in system parameters can move the electrode out of the electropolishing regime. When the rate of stirring is increased from a setting of #2 to #3 on the dial, surface etching and aggressive hemispherical pitting become apparent [Fig. 7(c)]. In addition, when the electrolyte concentration decreases from 600 to 200 g/L, severe pitting and general etching occur similar to what we observed at 0.3 A/cm^2 [Fig. 7(d)].

Stirring affects electropolishing by the following mechanism. An increase in stirring improves mass transport from the electrode surface. When the ferric nitrate falls below saturation, the salt film dissolves and electropolishing ceases.

A higher electrolyte concentration favors electropolishing in two ways. According to Eq. 7, a higher conductivity will increase the current density at the middle of the sample for the same average current density. A higher rate of dissolution increases ferric nitrate concentration at the central area to increase the size of the region where electropolishing can occur. In addition, solubility of ferric nitrate is dependent upon nitrate concentration in solution. As the nitrate concentration increases, ferric nitrate solubility decreases, thus favoring salt film formation.

These results may be compared with the findings reported by Wedman et al. who observed greater surface roughening for current densities above $0.1\text{--}0.2 \text{ A/cm}^2$.¹ This is in general agreement with the higher pitting that we saw in this study at $0.3\text{--}0.5 \text{ A/cm}^2$ compared with 0.05 A/cm^2 . Wedman et al. reported no measurements at 0.05 A/cm^2 in neutral-to-alkaline solution to compare with our results. Also, Wedman et al. did not make measurements above 0.5 A/cm^2 , the level at which classical electropolishing is encountered. Thus, inconsistencies between the two studies may be attributed to measurements made under different conditions.

Fig. 5(a). SC03 (center of specimen) slight pitting with general etching, grains apparent (x200): 200 g/L NaNO_3 , pH = 7, Cr^{+6} = 0.01 g/L, 0.05 A/cm², stirring rate #2.

Fig. 5(c). SA02 (center of specimen) numerous hemispherical and deep pits (x200): 600 g/L NaNO_3 , pH = 10, Cr^{+6} = 0.01 g/L, 0.05 A/cm², stirring rate #2.

Fig. 5(b). SB05 (center of specimen) hemispherical pitting and some deeper pits, surface etching (x200): 600 g/L NaNO_3 , pH = 7, Cr^{+6} = 0.01 g/L, 0.05 A/cm², stirring rate #2.

Fig. 5(d). SB01 (center of specimen) small pits and general etching (x200): 600 g/L NaNO_3 , pH = 10, Cr^{+6} = 12.5 g/L, 0.05 A/cm², stirring rate #2.

Fig. 6(a). SB03 center of electrode with extensive pitting, little surface etching (x200): 600 g/L NaNO_3 , pH = 7, Cr^{+6} = 0.02 g/L, 0.3 A/cm², stirring rate #3.

Fig. 6(c). SC02 center of electrode with surface etching and shallow pitting around 15 μM deep (x200): 200 g/L NaNO_3 , pH = 7, Cr^{+6} = 0.004 g/L, 0.3 A/cm², stirring rate #2.

Fig. 6(b). SB04 center of electrode with multiple shallow and deep pits, many 30–60 μM deep, little surface etching (x200): 600 g/L NaNO_3 , pH = 7, Cr^{+6} = 0.03 g/L, 0.3 A/cm², stirring rate #2.

Fig. 6(d). SC07 center of electrode with surface etching and shallow pitting around 15 μM deep (x200): 200 g/L NaNO_3 , pH = 10, Cr^{+6} = 0.04 g/L, 0.3 A/cm², stirring rate #2.

Fig. 7(a). SB02 (edge of specimen) electropolished area (x200)
600 g/L NaNO₃, pH = 7, Cr⁺⁶ = 0.01 g/L, 3.1 A/cm², stirring rate #2.

Fig. 7(b). SB02 (center of specimen) electropolishing still active in
darker area, grain boundaries and hemispherical pits (x200)
apparent, conditions same as above.

Fig. 7(c). SA06 (center of specimen) hemispherical pitting, surface
etching (x200): 600 g/L NaNO₃, pH = 10, Cr⁺⁶ = 0.004 g/L, 5 A/cm²,
stirring rate #3.

Fig. 7(d). SC04 (center of specimen) shallow pitting, general etching,
and a few deep pits (x200): 200 g/L NaNO₃, pH = 7, Cr⁺⁶ = 0.01 g/L,
3.1 A/cm², stirring rate #2.

Weld Zone Electrodisolution

We observed that approximately twice as much material was removed from the cans with exposed weld zones. The exposed weld zones were attacked very aggressively and the resulting surface texture was highly pitted. The affected weld zones were approximately 1/4-in. wide along the rim of the cans. This corresponds to half of the mass removed from about 6% of the total surface area.

Material removal from the can surface appeared to be in the etching mode. The mass dissolution rate from the can surface was $0.036 \text{ mg/cm}^2/\text{min}$ compared with $0.547 \text{ mg/cm}^2/\text{min}$ along the weld zones. For the duration of our tests, the trend for mass removal as a function of time for both conditions was linear. Test results are summarized in Fig. 8.

Fig. 8. Relative rates of dissolution of whole can and weld zones in sodium nitrate electrolyte.

Current efficiency for the tests with shielded weld zones was about 9% compared with 17% when the welds were exposed. Both values are lower than 20–30 % current efficiency seen in beaker tests at approximately the same current density and concentrations. The reason for the difference between the two test configurations is unclear.

The mechanism for enhanced mass removal on the weld zone is not completely understood. However, based on beaker tests with coupons of similar geometry, we believe that the change in the electric field at the corner is not a significant factor. It appears that the metallurgy of welded regions leads a higher surface energy which improves dissolution kinetics.

IMPLICATIONS

We explored a wide range of operating parameters for the nitrate system. Classical electropolishing is only reached in the nitrate system at current densities above 1 A/cm². Because of the large area of the cans (~1000 cm²) and limited power feedthroughs generally available in gloveboxes, the corresponding currents do not appear to be practical.

We obtained the next-best finish at approximately 0.05 A/cm² at lower electrolyte concentrations. While we obtained reasonable finishes, preferential attack at the welds is apparent. Another concern we had with the nitrate system is the added complexity of an electrolytic method to reduce Cr⁺⁶ for removal. Ferrous sulfate or sodium bisulfite may be used in the sulfate system without contamination of the electrolyte. In contrast, chemical reducing agents in the nitrate system contaminate the electrolyte.

Concurrent to our development work on the nitrate system, the sulfate system was being explored under the direction of the Laboratory's Doug Wedman. Tests using the sulfate system show that a 0.2-M (26.4 g/L) solution does not show preferential attack of weld zones. In addition, numerous chemical reducing agents for chromium are available that do not contaminate a sulfate bath. Therefore, we recommend that the sulfate electrolyte system be developed further.

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