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CORROSION RESISTANCE OF VARIOUS HIGH CHROMIUM ALLOYS
IN SIMULATED CHEMICAL PROCESSING NUCLEAR PLANT WASTE SOLUTIONS

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ABSTRACT

High chromium nickel alloys were tested at the Idaho Chemical Processing Plant (ICPP) to determine their corrosion performance in the high temperature aggressive chemical environments of liquid waste evaporators used in the chemical reprocessing of irradiated nuclear fuels. The results of these tests, which included a variety of base metal alloys / weld filler material combinations, are presented and discussed.

Keywords: Radioactive waste, nuclear fuel reprocessing, high chromium nickel alloys, super alloys, process evaporators, nitric acid, nitrates, fluorides, chlorides, sulfates, dissolved corrosion products, low pH, acidic liquid waste, alloy 33, UNS R20033, alloy G-30, UNS N06030

INTRODUCTION

During the last 50 plus years of the nuclear age, the United States alone has generated over 30,000 metric tons of spent nuclear fuel from power reactors, over 380,000 cubic meters of radioactive high level solid wastes, and 110 million gallons of high level radioactive liquid wastes. Spent (or "irradiated") nuclear fuels owned by the United States government were chemically reprocessed at the Idaho Chemical Processing plant (ICPP) from 1954 to 1991. The

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processes included dissolving the entire fuel elements in nitric and/or hydrofluoric acids followed by the liquid-liquid extraction separation of uranium from the fission products. The resulting high level liquid waste (HLLW) is, in some cases, concentrated in an HLLW evaporator, and solidified by calcining. The dry granular calcined waste contains the fission products as a variety of metal oxides that can ultimately be vitrified into a glass form for disposal in a geological repository. The ICPP also has a Liquid Effluent Treatment and Disposal (LET&D) facility for the recovery of nitric acid from selected process waste solutions. Other liquid wastes from the chemical processes are concentrated in the Process Equipment Waste (PEW) evaporator before they are sent to storage and ultimately to be calcined. This paper presents the results of several series of cyclic immersion corrosion tests that were conducted to determine the corrosion performance of various high chromium alloy/weld combinations in chemical environments similar to those encountered in process waste evaporators at the ICPP.

DESCRIPTION OF TEST PROGRAM

General

The reprocessing of spent nuclear fuel and management of the waste products can involve some very aggressive chemicals. Typical chemical media include a very low pH, high fluorides, high nitrates, sulfates and other corrosive species. The processes at the ICPP also contain low levels of chlorides which are present as impurities in process chemicals. Since some process solutions contain significant levels of radionuclides, radiological safety practices must be observed along with the usual chemical safety precautions; hence, materials performance with respect to the corrosion and integrity of process vessels, lines, etc. is extremely important. Since the ICPP first operated in the 1950's, there has been a program in place to monitor and evaluate the corrosion performance of the alloy/weld combinations in operating facilities in order to estimate their service lives. In addition, there are continuous efforts to identify new and improved alloy/weld combinations as they become available and to qualify them as possible replacement materials for repair and maintenance and allow for optimum material selection for future systems.

Tests

Several series of cyclic immersion tests have been conducted to evaluate the efficacy of high chromium nickel alloys to withstand corrosion in some of the current and possible future process waste solutions at the ICPP.^{1,2} Three evaporator facilities at the ICPP routine process extremely corrosive chemical media. They are the Process Equipment Waste (PEW) evaporator, the Liquid Effluent Treatment and Disposal (LET&D) evaporator, and the High Level Liquid Waste (HLLW) evaporator. The plant process solutions that are evaporated (boiling temperatures) in each of these facilities were simulated for corrosion testing with solutions having the chemical compositions presented in Table 1. All of these compositions are based on actual process conditions, but also represent the highest expected levels of acid and chloride and thus the most severe corrosive conditions. It should be noted that chloride is present only as an impurity in process chemicals, i.e. hydrochloric acid or other chloride compounds are not themselves introduced or added as actual process chemicals at the ICPP.

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Alloys

A variety of base alloy/weld metal combinations were corrosion tested in several series of cyclic immersion tests. The compositions of the individual base metal alloys and weld metals used in these studies are presented in Table 2. All coupons were welded, prepared for corrosion testing and otherwise handled as prescribed by ASTM procedures and then exposed to boiling test solutions under full reflux.

Initial tests with the PEW test solution disclosed that the G-30/IN-72 weld combination provides better corrosion resistance than does G-30/G-30. In fact absence of weld attack on the IN-72 weldment was so impressive that the tests were extended to a total of 11 seven-day long immersion cycles to observe their performance for a longer period of time. Only general attack was evident until the last half of the eleven cycles, during which time slight, but distinct penetrations appeared on the solidification lines of the weld. IN-72 welds were superior to the G-30 welds as shown in the general corrosion rates from eleven immersion cycles presented in Table 3.

A new alloy 33 (UNS R20033) was selected for testing because it was believed that due to its higher chromium content, it might provide better corrosion resistance in acidic high nitrate/fluoride solutions than any of the alloys already tested or in service at the ICPP. Previously published corrosion data, presented in table 4, indicate its superior resistance to corrosive attack by nitric and hydrofluoric acids and mixtures thereof.³ Based on this information and the availability of test specimens, welded alloy 33/IN-72 filler metal combination was selected for testing in cyclic corrosion tests at the ICPP along with the other alloy/weld combinations already in service or available for testing.

A matrix of the alloy/weld combinations tested at the ICPP and the simulated process solutions to which each was exposed are presented in Table 5. Not all alloy/weld combinations were tested under all possible conditions. All tests were conducted at boiling temperatures that were not measured, but are estimated to be 105°C for PEW solutions and 115°C for the LET&D and HLLW solutions at the 4,900 foot elevation of the test site in Idaho, where the boiling temperature is approximately 5°C lower than at sea level.

TEST RESULTS AND DISCUSSIONS

Alloy 33/IN-72 Test Samples

Alloy 33 welded with IN-72, which is a very high Ni-Cr alloy (56% Ni - 43% Cr), was tested for 5 seven day long cycles in each of the three test solutions described in Tables 1 and 5.

The general corrosion rates are presented in Table 6. As is evident, the general corrosion rates of the "as received" and the "machined and polished" coupons tested together in each solution were not significantly different and were quite low. In the PEW boyttoms solution, the

"as received" coupon exhibited only general attack except for several cracks from the weld/plate interface through the heat affected zone. The cracks were categorized as "liquation" cracks. These cracks were present only in one location of the "as received" specimen. They did not appear on the machined and polished specimen, which exhibited only general attack in PEW bottoms solution.

The alloy 33/IN-72 coupons exposed to the LET&D bottoms experienced extensive intergranular attack on all surfaces. The "as received" coupon exhibited small lines defining grain boundary attack extending down the sloped surfaces of the welds as well as distinct liquation cracks at the weld/plate boundary. The weld was also significantly discolored. The machined and polished coupon exhibited only intergranular attack. There were no cracks present.

Both alloy 33/IN-72 specimens exposed to concentrated HLLW solution exhibited general attack and some discoloration of the welds. The convex portion of the weld on the "as received" coupon had some small holes that appeared to be weld porosity, which could have occurred during preparation of welded samples.

Alloy G-30/"New G-30"

All tests with alloy G-30 welded with the "new G-30" combination were run in duplicate. The duplicate specimens were welded by different welders. The "new G-30" weld wire is a variation of G-30, containing approximately 34% Cr instead of typical 29%. The general corrosion rates presented in Table 7 are for seven 7 day long cycles, except for the LET&D bottoms solution, where test was stopped after the fourth cycle.

The coupons exposed to PEW solution exhibited only general attack for. At the end of seven 7-day cycles they showed slight indications of intergranular attack, especially on solidification lines in the welds. The corrosion rate of the two specimens were essentially similar.

The coupons exposed to high nitric acid LET&D bottoms solution showed extensive intergranular attack and discoloring on all surfaces in the fourth 7-day cycle. Apparently dissolved Cr was oxidized to Cr^{+6} in the boiling 12M HNO_3 , thereby greatly accelerating intergranular attack. These tests were later repeated with shorter cycles to prevent such high levels of dissolved Cr from accumulating. The results are presented in Table 8. After six cycles averaging 102 hours per cycle, the G-30/"new G-30" showed mild intergranular attack on the plate, less on the weld and a small, but definite enhanced local attack on the plate/weld metal interface. The welds also showed slight localized attack on the solidification lines.

The alloy G-30/"new G-30" coupons exposed to concentrated HLLW evaporator solution exhibited general attack on all surfaces, slight grain boundary attack in the plate only and significant weld discoloration. The weld of only the second coupon showed a slight enhancement of weld attack on solidification lines.

Alloy G-30/G-30 and Alloy G-30/IN-72

Another series of tests was run comparing alloy G-30/G-30 and alloy G-30/IN-72 combination. These were tested in a more "realistic" and less conservatively aggressive formulation of HLLW than the "worst case" composition presented in Table 1. The more realistic test solution is the same composition as indicated in Table 1, but with additional aluminum nitrate added to complex free fluoride ions and to bring the $[Al^{+3}]/[F^-]$ ratio into the range of 3.4 to 12⁽⁴⁾. The solution used for these tests was adjusted to the conservatively aggressive end of the complexing range, i.e. $[Al^{+3}]/[F^-]$ ratio of 3.4. That means that the fluoride in these tests is considerably more complexed and, therefore, should be less corrosive than the solution described in Table 1 with $[Al^{+3}]/[F^-]$ ratio of 1.18.

The general corrosion rates for alloy G-30/G-30 and G-30/IN-72 in boiling complexed HLLW evaporator bottoms solution are presented in Table 9. Interestingly, these rates are somewhat higher than those for a similar alloy/weld combination (G-30/"new" G-30) reported in Table 7 for conservative "worst case" HLLW solution (Table 1). Also the corrosion rates on the as received sample was higher than the machined and polished specimens. The difference may be attributed to the substantially higher nitrate concentration (9.5 M vs. 7.5 M) from the additional aluminum nitrate in the fully complexed solution or somewhat higher boiling temperatures. Also, these rates are somewhat lower than reported for the similar alloy/weld combination in LET&D bottoms solutions in Table 8, which again may be attributed to differences in nitrate concentrations (9.5 M vs. 12.0 M) or boiling temperatures. Both the plate and the weld portions of G-30/G-30 exhibited intergranular attack in boiling complexed HLLW. The attack at the interface was especially severe. In addition small holes were observed in the weld, apparently from attack of the high Cr-Mo secondary phase. The G-30 plate portion of the G-30/IN-72 combinations exhibited exactly the same intergranular attack as seen in the G-30/G-30 specimens. The IN-72 welds performed much better, with little if any intergranular attack. The only observed change in the welds was its discoloration.

CONCLUSIONS

Based on the premise that base metal and weldment are generally considered to be satisfactory for plant service if they exhibit low general corrosion rates of less than 4 mpy with no significant localized attack, the acceptability of the alloy/weld combinations in the current tests can be summarized and concluded as follows:

- o Alloy 33 / IN-72 - satisfactory for PEW and HLLW, but not for (extremely high nitric acid) LET&D service
- o Alloy G-30/"new" G-30 - satisfactory for PEW, but borderline for HLLW and unsatisfactory for LET&D service.
- o Alloy G-30/IN-72 - the plate was unsatisfactory for realistic (complexed and also high nitrate) HLLW. However, the IN-72 weld material performed well.

- o Alloy G-30/G-30 - here neither the plate nor the weld held up in complexed, high nitrate HLLW service.
- o High nitrate concentrations ($>8M$) tend to oxidize any Cr(III) corrosion product to Cr(VI), which in turn accelerates general corrosion and promotes intergranular attack. Alloy 33 in combination with IN-72 weld consumables appears to have a slight advantage over alloy G-30 in these series of tests.
- o Alloy 33 (UNS R20033) can be a cost effective alternative to alloy G-30 for potential applications in chemical reprocessing of spent nuclear fuel.

REFERENCES

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- 3) M. Köhler, et al, Alloy 33: A New Material for the Handling of HNO_3 /HF Media in Reprocessing of Nuclear Fuel, Corrosion/97, Paper # 115, (NACE International, Houston, Tx 1997)
- 4) R.E. Schindler, Lockheed Martin Idaho Technology Inc., Private Communication, June 1995

TABLE 1

Chemical Compositions of Simulated CPP Waste Solutions

PEW Evaporator Bottoms	1.0 <u>M</u> Na^+	5.0 <u>M</u> NO_3^-	0.041 <u>M</u> SO_4^{2-}
	0.107 <u>M</u> F^-	0.105 <u>M</u> Ca^{+2}	approx. 3 <u>N</u> H^+
	0.057 <u>M</u> Cl^-	0.111 <u>M</u> Al^{+3}	
LET&D bottoms	12.0 <u>M</u> HNO_3	0.05 g SO_4^{2-}/L	
	1.6g F^-/L	100 μ g Cl^-/ml	
	4.55 g Al^{+3}/L		
"Worst case" HLLW evaporator solution (WM-181 solution concentrated 2.5X)	2.0 <u>M</u> Na^+	7.5 <u>M</u> NO_3^-	0.025 <u>M</u> Cr^{+6}
	0.425 <u>M</u> F^-	0.0296 <u>M</u> Cl^-	approx. 6 <u>N</u> H^+
	0.50 <u>M</u> Al^{+3}	0.25 <u>M</u> K^+	

TABLE 2

Typical Chemistry of Alloys Used for Tests in
Idaho Chemical Processing Plant Process Solutions

<u>Base Alloy /</u>	<u>UNS No.</u>	<u>Ni</u>	<u>Cr</u>	<u>Mo</u>	<u>Fe</u>	<u>Cu</u>	<u>Others</u>
Alloy 33	R20033	31	33	1.6	32	0.6	N-0.4
Alloy G-30	N06030	Bal	29	5	15	1.6	W, Cb+Ta
<u>Filler Weld Alloy</u>							
IN-72	-	56	43	-	-	-	-
G-30	-	Bal	29	5	15	1.6	W, Cb+Ta
"New" G-30	-	Bal	34	5	15	1.6	W, Cb+Ta

TABLE 3

General Corrosion Rates of Welded Alloys Exposed
to Simulated PEW Bottoms Solution for Eleven 7-Day Cycles

<u>Alloy/Weld Combination</u>	<u>General Corrosion Rate, mils/year</u>
G-30/G-30, as welded	3.0
G-30/G-30, machined and polished	4.6
G-30/IN-72, as welded	2.6
G-30/IN-72, machined and polished	2.4

TABLE 4

Corrosion Performance on Alloys 33, G-30 and 690 in Nitric Acid and Nitric/HF Acid

Corrosion Rate (MPY) for Alloy 33
Nitric Acid Concentration

<u>75 %</u>		<u>85 %</u>		<u>90 %</u>		<u>95 %</u>	
<u>50°C</u>	<u>75°C</u>	<u>50°C</u>	<u>75°C</u>	<u>50°C</u>	<u>75°C</u>	<u>50°C</u>	<u>75°C</u>
<0.5	1	<0.5	3*	<0.5	7*	3*	14*

* Some intergranular corrosion

Corrosion Rate for Alloys 33, G-30 and 690 in
Nitric Acid and Hydrofluoric Acid MixtureCorrosion Rate (MPY) at 90°C

<u>Alloy</u>	<u>12% HNO₃ +0%HF</u>	<u>12% HNO₃ +0.9%HF</u>	<u>12% HNO₃ +3.5%HF</u>
33	<0.5	11	52
G-30	<0.5	12	53
690	<0.5	27	154

<u>Alloy</u>	<u>0.4 % HF +32% HNO₃</u>	<u>0.4 % HF +44.5% HNO₃</u>	<u>0.4 % HF +56% HNO₃</u>
33	12	30	73
G-30	22	64	105
690	46	87	206

TABLE 5

Alloy/Weld Combination Tests in ICPP Test Solution

<u>Alloy/Weld Combination</u>	<u>Test Condition (Solution)</u>
o Alloy 33 Welded with IN-72	- Process Equipment Waste (PEW) Evaporator Bottoms - Liquid Effluent Treatment and Disposal (LET&D) Bottoms - High Level Liquid Waste (HLLW) Evaporator Bottoms (under complexed)
o Alloy G-30 Welded with "new" G-30	Same as above except in the HLLW Evaporator Bottoms solution was conservative (under complexed)
o Alloy G-30 Welded with IN-72	HLLW Evaporator Bottom - Realistic (not under complexed)
o Alloy G-30 Welded with alloy G-30	HLLW Evaporator Bottom - Realistic (not under complexed)

Table 6

Corrosion Rates of Alloy 33/IN-72 in Boiling Waste Solutions, mils/yr

	<u>PEW Solution</u>		<u>LET&D Bottoms</u>		<u>Concentrated HLLW</u>	
<u>(7 day cycles)</u>	<u>As rec'd</u>	<u>Machined and polished</u>	<u>As rec'd</u>	<u>Machined and polished</u>	<u>As rec'd</u>	<u>Machined and polished</u>
Cycle I	1.45	1.33	12.1	11.9	1.80	1.45
Cycle II	0.82	0.79	7.8	8.3	1.51	1.58
Cycle II	0.83	0.78	7.8	8.1	1.94	1.94
Cycle IV	1.06	1.18	6.0*	6.4*	1.99	1.87
Cycle V	1.05	0.97	8.3	8.7	2.10	1.81
Average	1.04	1.01	9.0	9.2	1.87	1.73

*Blew fuse in heating mantle over a weekend during Cycle IV. Heat was off an unknown amount of time, hence values are really > 6.0 and > 6.4 mpy. These numbers were not included in the calculated average rates

Table 7

Corrosion Rates of Alloy G-30/"New G-30"
in Boiling Waste Solutions, mils/yr

(7 day cycles)	<u>PEW Solution</u>		<u>LET & D bottoms</u>		<u>Concentrated HLLW</u>	
	#1	#2	# 1	#2	#1	#2
I						
II	2.2	1.3	7.1	7.8	2.1	2.0
II	1.6	1.6	5.6	5.4	0.4	0.3
III	1.5	1.8	6.6	6.2	0.7	0.6
IV	1.0	1.1	131*	120*	0.3	0.4
V	0.8	0.7	-	-	2.2	1.8
VI	0.8	0.7	-	-	1.8	1.8
VII	0.7	0.7	-	-	1.8	1.8
Average	1.2	1.1			1.3	1.2

*Excessive intergranular attack. These tests were repeated with shorter cycles. However, it should be noted that such conditions could occur in the LET & D operating under full reflux with no feed.

TABLE 8

Corrosion Rates (mpy) of Alloy G-30/"New G-30"
In Boiling LET&D Bottoms Solution, Shorter Exposure Time

<u>Cycle # (length, hrs)</u>	<u># 1</u>	<u>#2</u>
I (168)	10.8	11.3
II (72)	8.6	8.7
III (96)	8.7	8.2
IV (113)	8.6	8.5
V (74)	8.7	8.2
VI (92)	8.5	8.2
Average	9.0	8.9

Table 9

Corrosion Rates of Alloy G-30/G-30 and G-30/IN-72 in Realistic*
Boiling HLLW Evaporator Bottoms Solution, mils/yr

<u>Cycle number/ length of test, hrs</u>	<u>Alloy G-30/G-30</u>		<u>Alloy G-30/IN-72</u>	
	<u>Machined & polished</u>	<u>As Received</u>	<u>Machined & polished</u>	<u>As Received</u>
I/116	2.9	5.6	3.1	6.1
II/145	3.2	4.7	2.3	5.8
III/140	3.1	4.4	3.4	5.0
IV/169	2.7	3.7	3.1	4.7
V/164	2.7	3.6	3.0	3.8
Average	2.9	4.4	3.0	5.1

*Less conservatively aggressive - see text for explanation

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