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AN EVALUATION OF THE CRYOFIT® TUBE
JOINING SYSTEM IN SELECTED
PLUTONIUM CHEMICAL PROCESSING SOLUTIONS

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SUBJECT DESCRIPTORS

Corrosion
Materials of Construction
New Materials Laboratory Testing
Titanium Alloys

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AN EVALUATION OF THE CRYOFIT® TUBE JOINING SYSTEM IN SELECTED PLUTONIUM CHEMICAL PROCESSING SOLUTIONS

James M. Macki, Kazuji Terada, and Robert L. Kochen

Abstract. The Ni-Ti alloy Cryofit® joining system has been evaluated for corrosion resistance to selected solutions encountered in the chemical processing of plutonium. Results indicated the Cryofit system has useful resistance to $\text{Al}(\text{NO}_3)_3$, $\text{H}_2\text{C}_2\text{O}_4$, KOH , and very dilute H_2SO_4 . The Cryofit system is not suitable for HNO_3 service or for NH_4SCN service when used with 304 stainless steel.

INTRODUCTION

The Cryofit®* tube fitting system has been proposed as a tube joining system to replace the Teflon®-gasketed flanged joints for handling some plutonium solutions.

The Cryofit tube fitting system provides a means of connecting tubes and pipes without flanges, welds, or elevated temperatures. Permanent connections are made by removing a Cryofit coupling from liquid nitrogen and inserting the tubes to be joined into the ends of the coupling. As the coupling warms from liquid nitrogen to room temperature, it shrinks onto the tubing with tremendous force generated by internal stresses.

This contraction while warming is the feature of the Cryofit coupling which makes the system work. Contraction is due to the "memory" characteristic of the Ni-Ti alloy from which the couplings are manufactured. The alloy can be deformed at cryogenic temperatures and will retain this deformation until the material is allowed to warm to the transformation temperature. Upon transformation, the material will attempt to return to its original dimensions by generating stresses exceeding 100,000 psi.

The Cryofit system provides highly reliable joints which are being used in aircraft and space vehicle

hydraulic systems. The suitability of Cryofit joints for chemical plant operations has not been previously evaluated or even considered.

This investigation was undertaken to evaluate the corrosion resistance of Cryofit-joint material when subjected to some plutonium processing solutions.

SUMMARY AND CONCLUSIONS

The results of this investigation show that the Cryofit joint could be useful for joining 304 stainless steel conduit carrying 0.3M H_2SO_4 , 3.1M $\text{Al}(\text{NO}_3)_3$, 0.5M $\text{H}_2\text{C}_2\text{O}_4$, and 6M KOH . Because of the detrimental galvanic corrosion effect on 304 stainless steel, the Cryofit joints are not suitable for 6.2M NH_4SCN service. Cryofit joints are also unsuitable for nitric acid service.

EXPERIMENTAL

Screening Tests

Raychem Corporation used a Cryofit sleeve to join 0.5-in.-diameter 304 stainless steel tubes for screening-corrosion tests. The steel tubes were cut so $\frac{1}{2}$ in. extended from each end of the sleeve.

The outside diameter of each tube and Cryofit sleeve was measured before and after the corrosion tests. Each joint was cleaned with acetone, dried, weighed to the nearest 0.1 mg and immersed in 400 ml of the test solution. After either one hour or 168 hours, the joints were removed from the solution, rinsed in water and acetone, dried, and reweighed. The test solutions used for the screening tests were 7M HCl , 7M HNO_3 , 12M HNO_3 + 0.6M HF , and 6M KOH . All of the tests were at room temperature ($26 \pm 2^\circ\text{C}$).

*Manufactured by Raychem Corporation, Menlo Park, California.

All test times were seven days (168 hours) except for the 7M HCl tests which were limited to one hour because of the rapid reaction rate.

Gravimetric Immersion Tests

Additional gravimetric-immersion and galvanic-gravimetric-corrosion tests were conducted using Cryofit alloy and 304 stainless steel disks. The Cryofit alloy disks were machined from sheet materials supplied by Raychem Corporation.

All disks were polished with 240 grit silicon-carbide paper. The polished 304 stainless steel disks were passivated by pickling in 10 vol% H₂SO₄ for 5 minutes, rinsing in distilled water, and drying in air. This treatment ensured that the stainless steel specimens were uniformly passivated.¹ The passivated stainless steel disks and the polished Cryofit alloy disks were measured with a micrometer, acetone cleaned, and weighed to the nearest 0.1 milligram.

Gravimetric-immersion tests were conducted following National Association of Corrosion Engineers (NACE) standard test method TM-01-69. The procedures involved individually immersing weighed Cryofit alloy disks in 400 ml of test solution contained in a 500-ml-tall-form beaker with a petri disk cover to control evaporation. The disks were supported by a glass holder which positioned each specimen about 25 mm from the bottom of the beaker, inclined about 30° from the vertical.

The covered beakers holding the specimens were placed in a furnace maintained at 50 ± 2°C for 720 hours (30 days). The tests in 12M HNO₃ + 0.6M HF + 0.6M Al(NO₃)₃ were terminated after 72 hours because of rapid corrosion reaction.

After 720 hours of exposure, the specimens were rinsed in water, dried, and reweighed. Weight losses were used to calculate the corrosion rates in mils penetration per year (mpy) using the expression

$$\text{mpy} = \frac{(534)\Delta W}{\text{DAT}}$$

where ΔW is the weight loss in mg, D is the density in g/cm³, A is the surface area in square inches, and T is the exposure time in hours.

Galvanic-Gravimetric Tests

Galvanic-gravimetric tests were conducted to determine the effects of galvanically coupling 304 stainless steel and the Cryofit alloy in some process solutions. The disk-shaped specimens were prepared and weighed in the same manner as the gravimetric-immersion tests.

The weighed disks were assembled into galvanic couples by mounting them in a nylon holder similar to a C-clamp. Couples were made by clamping a stainless steel disk and Cryofit alloy disk together with nylon screws and coating the exposed edges of the disks with silicon adhesive (Dow Corning 3145) so that only one face of each disk was exposed to the environment. The electrical resistance of each couple was checked before and after exposure to ensure electrical contact between the disks. The adhesive required 24 hours to set, so the couples were exposed to laboratory air for 24 to 30 hours prior to exposure to the test solutions. The galvanic couples were immersed in 400 ml of test solution in a covered tall-form beaker and placed in a furnace maintained at 50 ± 2°C for 30 days. At the end of the exposure period, each couple was disassembled and the silicone adhesive stripped off.

The disks were rinsed in distilled water and acetone, then dried and reweighed to determine weight losses. The weight losses were used to calculate the corrosion rates as mpy in the same manner as the gravimetric-corrosion rates.

Electrochemical Measurements

Galvanic potentials generated by electrodes fabricated from Cryofit alloy disks and passivated 304 stainless steel disks were measured versus a saturated calomel electrode using an electrometer.

RESULTS AND DISCUSSION

The Rocky Flats Analytical Laboratories examined a sample of a Cryofit sleeve and reported that the alloy contained 58.9 wt% Ti, 36.9 wt% Ni, 3.6 wt% Fe, and 0.5 wt% Sn. Results of the spark mass spectrographic analysis of the Cryofit sleeve material are summarized in Table 1.

Results of the screening-corrosion tests are shown in Table 2. These results indicated the Cryofit joints might be suitable for nitric acid and potassium hydroxide service.

Table 1. Results of Spark Mass Spectrographic Analysis of a Cryofit Sleeve.^a

Element	ppm	Element	ppm
Al	4	Na	4
As	34	Nb	18
C	38	Ni	(36.9 wt%)
Ca	29	P	3
Cl	3	S	79
Co	146	Sb	89
Cr	90	Si	5
Cu	178	Sn	(0.5 wt%)
Fe	(3.6 wt%)	Ti	(58.9 wt%)
K	10	Zn	36
Mn	27	Zr	22
Mg	5		

^aThe wt% values in parentheses were obtained from atomic absorption analysis.

Results of the gravimetric-corrosion tests shown in Table 3 indicate the Cryofit alloy has useful corrosion resistance in 3M HNO₃ and is resistant to 0.3M H₂SO₄, 3.1M Al(NO₃)₃, 0.5M H₂C₂O₄, 6.2M NH₄SCN, and 6M KOH (50°C). These results also show that 0.02M H₂SO₄ added to 7.5M HNO₃ decreases the corrosion rate by a factor of 3 even though 3M H₂SO₄ proved to be the most corrosive solution tested. All corrosion rates in 7.5M and 12M HNO₃ were about 30 mpy which would preclude the use of Cryofit joints in these acids.

The effects of galvanically coupling the Cryofit alloy to 304 stainless steel are summarized in Table 4 and Table 5. The galvanic-potential measurements in Table 5 show the Cryofit alloy is anodic to 304 stainless steel in all test solutions except 0.3M H₂SO₄ and 6M KOH. In the remaining solutions, the Cryofit alloy should corrode preferentially when coupled to 304 stainless steel (cathodic protection). Results identified in Table 4 show the Cryofit alloy corrodes in most solutions as would be predicted by the galvanic-potential measurements. The Cryofit alloy corrosion rate is not affected, however, by 304 stainless steel in 0.3M H₂SO₄ even though 304 is anodic in the 25°C solution. The galvanic potentials were measured in 25°C solution and the galvanic-gravimetric tests were conducted in 50°C solution so some discrepancies should occur between Tables 4 and 5.

Table 2. Results of the Room Temperature (26 ± 2°C) Screening Corrosion Tests on Cryofit Joints.^a

Solution	Test Time (hours)	Initial Weight ^b (grams)	Weight Change ^b (milligrams)	Cryofit o.d. Change ^c (mils)	Comments
7M HCl	1	33.0384	- 137.1	- 1.0	Visible corrosion on Cryofit
7M HCl	1	32.7985	- 112.2	- 2.0	Visible corrosion on Cryofit
7M HNO ₃	168	33.1863	- 12.8	< 0.5	No visible attack
7M HNO ₃	168	32.7833	- 19.9	< 0.5	No visible attack
12M HNO ₃ + 0.6M HF	168	33.0102	- 2,637.2	-15.0	Visible corrosion on Cryofit
12M HNO ₃ + 0.6M HF	168	32.3200	- 2,692.5	-15.0	Visible corrosion on Cryofit
6M KOH	168	32.3830	+ 4.6	< 0.5	Brown tarnish on Cryofit
6M KOH	168	32.4043	+ 1.8	< 0.5	Brown tarnish on Cryofit

^aEach joint consisted of two pieces of 304 stainless steel tubing (0.50 in. o.d. by 1.15 in. long) joined together with a 1.30-in.-long Cryofit couple.

^bInitial weight and weight change of entire joint including stainless steel tubes and Cryofit couple.

^cThe accuracy of the outside-diameter measurement was ±0.5 mil.

Table 3. Gravimetric-Corrosion Test Results for Cryofit Alloy Disks in Selected Process Solutions.^a

Solution	Weight Loss (milligrams) ^b	Corrosion Rate (mpy) ^c
3M HNO ₃	168.7	11
3M HNO ₃	174.7	12
7.5M HNO ₃	440.9	30
7.5M HNO ₃	413.3	28
12M HNO ₃	446.4	30
12M HNO ₃	456.9	31
7.5M HNO ₃ } + 0.2M H ₂ SO ₄ }	134.6	9
	130.0	9
0.3M H ₂ SO ₄	39.8	3
0.3M H ₂ SO ₄	40.2	3
3M H ₂ SO ₄	(Disks dissolved in 200, 300, 350, and 600 hours)	
12M HNO ₃ } +0.6M HF }	1843.0	1300 ^d
	1881.4	1300 ^d
+0.3M Al(NO ₃) ₃ }		
6.2M Al(NO ₃) ₃	3.6	0.2
6.2M Al(NO ₃) ₃	6.7	0.4
0.5M H ₂ C ₂ O ₄	71.2	5
0.5M H ₂ C ₂ O ₄	68.8	5
6.2M NH ₄ SCN	0	0
6.2M NH ₄ SCN	0	0
6M KOH	0	0
6M KOH	0	0

^a50 ± 2°C, 720-hour tests unless otherwise noted.^bThe initial weight of the disks was about 4 grams.^cmpy – mils penetration per year.^d72-hour tests.

Although 304 stainless steel has a reported² corrosion rate of less than 2 mpy in 6.2M NH₄SCN at 50°C, the corrosion rate is about 60 mpy when 304 is galvanically coupled to the Cryofit alloy.

REFERENCES

1. M. G. Fontana, *Industrial and Engineering Chemistry*, 39, 103A (1957).
2. *Corrosion Data Survey*, 1967 Edition, National Association of Corrosion Engineers, Houston (1968).

Table 4. Galvanic-Gravimetric Corrosion Rates^a for the Galvanic Cell:

CRYOFIT ALLOY \ SOLUTION \ 304 STAINLESS STEEL	Corrosion Rate (mpy) ^b	
	Cryofit	304
Solution		
3M HNO ₃	32	0
3M HNO ₃	29	0
7.5M HNO ₃	73	0
7.5M HNO ₃	76	0
12M HNO ₃	79	0
12M HNO ₃	82	0
7.5M HNO ₃ } +0.02M H ₂ SO ₄ }	29	0
	26	0
0.3M H ₂ SO ₄	4	0
0.3M H ₂ SO ₄	3	0
3.1M Al(NO ₃) ₃	0.2	0
3.1M Al(NO ₃) ₃	0.3	0
0.5M H ₂ C ₂ O ₄	3	0.3
0.5M H ₂ C ₂ O ₄	4	0.6
6.2M NH ₄ SCN	0	59 ^c
6.2M NH ₄ SCN	0	56 ^c
6M KOH	0	0
6M KOH	0	0

^a50 ± 2°C, 720-hour tests unless otherwise noted.^bmpy – mils penetration per year.^c192-hour tests.**Table 5. Galvanic Potentials of Cryofit Alloy and 304 Stainless Steel in Test Solutions at 25°C.^a**

Solution	Potential (volts vs. SCE) ^b	
	Cryofit	304
3M HNO ₃	+0.145	+5.60
7.5M HNO ₃	+4.40	+6.55
12M HNO ₃	+5.78	+8.20
7.5M HNO ₃ } +0.02M H ₂ SO ₄ }	+0.235	+7.05
0.3M H ₂ SO ₄	+0.115	+0.025
3M H ₂ SO ₄	+0.127	+0.145
12M HNO ₃ } +0.6M HF }	+4.80	+8.10
+0.3M Al(NO ₃) ₃ }		
3.1M Al(NO ₃) ₃	+0.110	+4.98
0.5M H ₂ C ₂ O ₄	+0.910	+4.30
6.2M NH ₄ SCN	+0.921	+3.65
6M KOH	+0.790	-0.210

^aThe more positive potential corresponds to the more noble metal in each environment.^bSCE – saturated calomel electrode.