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MATERIALS FOR FLUORINE GENERATOR ANODE ASSEMBLIES

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ABSTRACT

Corrosion of anode assembly materials in fluorine generators is pronounced, therefore, selection of the proper materials of construction is important. Several metals and alloys have been tested for corrosion resistance when anodic in a fluorine test cell. The relative corrosion resistance of most of the materials has been determined by three methods. The current-voltage method is the most rapid and, generally, is verified by the other two methods. By this method, current-voltage curves are obtained for the material under test. The corrosion is proportional to the current, therefore, the relative corrosion rate as a function of the voltage may be obtained by referring to the curve.

In general, copper, copper alloys and magnesium alloys offer the best corrosion resistance. The resistance of copper is improved by alloying with zinc, phosphorous, tin, beryllium and aluminum, but lead and silicon have the opposite effect. The resistance of mild steel is little changed by addition of alloying elements. High nickel alloys, lead, aluminum and cast iron were severely corroded. Several materials which offer good corrosion resistance at low voltages (i.e. 10 volts) were badly pitted at voltages above the breakdown voltage.

MATERIALS FOR FLUORINE GENERATOR ANODE ASSEMBLIES

Corrosion of anode assembly materials in fluorine generators is quite pronounced, and is believed to be one of the primary causes for cell failure, especially in long-lived cells. This makes the proper selection of materials of construction of prime importance. Tests have been made in the laboratory in order to evaluate a number of materials for possible use in fluorine generators.

The primary method of testing consisted of obtaining current-voltage data for the test materials when anodic in a pot of molten electrolyte. The relative corrosion resistance of the materials is assumed to be proportional to the current carried at any given voltage. The validity of this method of testing was determined by two other methods.

CONCLUSIONS

The relative corrosion resistance of a number of materials when anodic in a fluorine test cell has been determined. Several of the materials were tested by three different methods in order to evaluate the current-voltage method of predicting the corrosion resistance of a material. Although a few discrepancies are evident, generally, the materials tested hold their same relative position with respect to corrosive resistance regardless of the method of testing. The current-voltage method has the advantage that it is rapid and the corrosion rate as a function of voltage is easily predicted.

It was found that, in general, copper, copper alloys and magnesium alloys offer the best corrosion resistance. The resistance of copper is improved by alloying with zinc, phosphorous, tin, beryllium and aluminum, but lead and silicon have the opposite effect.

Ordinary mild steel would be classed as a material of secondary usefulness. In general, its resistance was unchanged or reduced by the addition of alloying elements.

A third class of materials showing little or no corrosion resistance included high nickel alloys, lead, aluminum and cast iron.

Several of the materials that offer good resistance at low voltages (i.e. 10 volts) were quite severely pitted at voltages above the breakdown voltage. In general, single phase alloys were not pitted, whereas multi-phase metals were attacked. With this in mind, of the materials with apparently good corrosion resistance, phosphorous-bronze, beryllium copper and aluminum bronze with less than 8% aluminum would deserve the best rating.

The fact that severe corrosion is observed on samples that have been tested at potentials above the breakdown voltage indicates that an inordinate amount of damage may be done to a cell if the conditioning procedure is prolonged at these voltages.

DISCUSSION AND EXPERIMENTAL

A rapid and convenient method for predicting the relative corrosion resistance of a material when anodic in a fluorine generator at various potentials is desirable; therefore, the first series of tests consisted of obtaining current-voltage data for the test materials. It was assumed that the corrosion rate would be proportional to the current. This assumption is verified, generally, in subsequent tests.

The cell for testing prospective anode assembly materials consisted of a steel pot eight inches in diameter, containing molten potassium bifluoride and hydrogen fluoride to an approximate depth of twelve inches. The steel pot served as the cathode and the material being tested as the anode. A direct current power source provided a maximum of ten amperes at forty-two volts. Current and voltage measurements were made with portable test meters which would introduce considerable error in the measurements at low readings, but all readings should be comparable. The hydrogen fluoride content of the electrolyte was maintained at $41 \pm 1\%$ and the temperature at $100 \pm 5^\circ\text{C}$. The water content of the electrolyte was less than 0.04% for all tests.

The test specimens for which the current-voltage data were obtained were $3/8$ inch rods unless otherwise specified. The data were obtained by immersing the rods to a depth of five inches in the center of the pot and rapidly increasing the voltage until the current reached ten amperes or the voltage reached the maximum. The voltage was then gradually decreased over a period of approximately one-half hour. The current-voltage curves obtained in this manner are given in Figure No. I.

From these curves it can be seen that the current increases pronouncedly as the voltage is increased. This suggests that a significant amount of the corrosion in production cells may occur during conditioning or polarization of the cells, at which time the voltage becomes considerably higher than the normal eight to ten volt operating range. For example, copper which carried a current of approximately 0.001 amperes at 10 volts carried 10 amperes at 33 volts. If this same relation holds in a cell with completely polarized carbons, in one hour at 33 volts corrosion of the copper would be equivalent to 40,000,000 ampere hours at the normal 4000 ampere operation. Obviously these conditions are not obtained, but this example is given in order to illustrate the order of magnitude of damage that may be done.

The materials tested by the current-voltage method are rated according to decreasing corrosion resistance in Table No. I. These ratings are based on a ten volt operating level except in the few cases indicated. It was of interest to note that the cast iron anode produced fluorine. By qualitative means it appeared that fluorine was produced at potentials as low as 4.0 - 4.5 volts. High carbon steel, however, does not produce noticeable amounts of fluorine. Also contained in Table No. I is the observed condition of some of the specimens after the current-voltage tests were made. Some of the samples are illustrated in Figure No. II. None of the pitting conditions recorded in this table occur at ten volts or less as is proved by additional tests.

Current-voltage curves have also been obtained for some of the materials listed in Table No. I using the test specimen as the cathode and a carbon rod as the anode. This information was obtained to determine if any of the materials would make poor cathodes. It is believed that a generator skirt material which would carry little current as a cathode would reduce the corrosion rate of anode assembly materials. The curve in Figure No. III represents the data for all materials tested, as no significant differences were noted. A list of the materials is given below:

Materials tested as cathodes - Copper DHP
Stainless Steel 304
Steel 4140
Steel 1020
Steel 1095
Free Cutting Brass
Monel
Lead
Aluminum 24S
Cast Iron
Phosphorous Bronze
Bearing Bronze
Tool Steel No. 10

In order to substantiate current-voltage measurements as a valid method of determining the relative corrosion rates of anodic materials, two additional methods of testing were utilized. The first of these consisted of determining the corrosion rate of some of the test materials acting as anodes at constant voltage. Again the test specimens were in the form of $3/8$ inch rods and were immersed to a depth of five inches in electrolyte. A potential of ten volts was applied, when possible, for the duration of the test. The data obtained by this test are recorded in Table No. II.

A further evaluation of the current-voltage method was made by determining the corrosion rate of a number of the materials acting as anode pressure plates. The specimens tested were plates having the dimensions $1/8$ " x 1" x $1-3/4$ ". These plates were bolted to a 1" x 1" x 8" carbon anode. Electrical contact was made directly to the test plate. The carbon anode was then suspended in a pot of electrolyte to a depth such that one square inch of each pressure plate was immersed in the electrolyte. A skirt was used in conjunction with the carbon anode so that an atmosphere of pure fluorine surrounded the exposed portions of the pressure plates. Conditions and results of the tests are contained in Table No. III.

A comparison of the corrosion resistance of all materials tested by the three methods of testing is given in Table No. IV. The materials are listed in order of decreasing corrosion resistance. Although a few discrepancies are evident, generally, the materials tested hold the same relative position regardless of the method of testing.

The chemical composition and some of the physical characteristics of the materials used in the various tests are given in Table No. V. The physical properties listed in this table are estimated from the actual condition of the metal as determined by hardness measurements.

Table No. I

CURRENT-VOLTAGE DATA

<u>Sample</u>	<u>Volts</u>	<u>Amperes</u>	<u>Surface Conditions of Sample After Test</u>
Cartridge Brass ⁽¹⁾	10	0.000029	Very rough
Phos. Bronze	10	0.000058 ⁽²⁾	Smooth
Free Cutting Brass	10	0.000060 ⁽²⁾	Very rough
Be Copper	10	0.00016	Etched
Silver Plate	10	0.00016 ⁽³⁾	Silver removed
Copper ETP	10	0.00022	Etched
Ampco 8	10	0.00043	Smooth ⁽⁴⁾
Ampco 45	10	0.00052	Smooth ⁽⁴⁾
Stainless Steel 410	10	0.00060	Smooth
Copper (DHP)	10	0.00090	Rough
Magnesium	10	0.0011	Very rough
Ampco 18	10	0.0030	Smooth ⁽⁴⁾
Bearing Bronze	10	0.0038	Severely pitted
Tool Steel 11 ⁽¹⁾	10	0.0075 ⁽²⁾	Pitted
Steel 1020	10	0.0075	Pitted
Everdur 1010 ⁽¹⁾	10	0.025	Severely pitted
Steel 1095	10	0.041	Pitted
Everdur 1010	10	0.054	Severely pitted
Tool Steel 10	10	0.055	Pitted
Steel 4140	10	0.12	Rough
Stainless Steel 304	10	0.49	Rough
Monel	7.4	10	-
Cast Iron	6.2	10	-
Lead	2.6	10	-
Aluminum	2.0	10	-

(1) 1/4 Inch Rod.

(2) Duplicate Sample.

(3) Silver removed shortly after test started, therefore, current at 10 volts is characteristic of copper not silver.

(4) Low amperage runs due to voltage limitations.

Table No. II

CORROSION RATE OF ANODE MATERIALS AT CONSTANT VOLTAGE

<u>Material</u>	<u>Duration of Test, Hrs.</u>	<u>Volts</u>	<u>Wt.Loss/Hr.,g.</u>
Free Cutting Brass	64	10	0.0018
Free Cutting Brass	16	10	0.0019
*Cartridge Brass	16	10	0.0036
Magnesium	16	10	0.0038
Copper ETP	16	10	0.0058
Copper DHP	16	10	0.0061
Bearing Bronze	16	10	0.0080
Tool Steel No. 10	16	10	0.008
Phos. Bronze	16	10	0.0098
Stainless Steel 410	16	10	0.010
Ampco 45	16	10	0.011
Steel 1020	16	10	0.0130
Ampco 18	16	10	0.013
*Everdur 1010	17	10	0.0132
*Be Copper	16	10	0.0137
Ampco 8	16	10	0.022
Steel 1095	64	10	0.034
Everdur 1010	16	10	0.0511
Silver Plated Cu	16	10	0.0863
Stainless Steel 304	16	10	0.158
Steel 4140	16	10	0.19
**Cast Iron	16	6.7	0.64
**Monel	16	7.0	0.72

*Test specimen was 1/4 inch rod immersed to a depth of 7-1/2 inches.

**Fluorine produced.

Table No. III

MATERIALS TESTED AS ANODE PRESSURE PLATES

<u>Material</u>	<u>Duration of Test, Hrs.</u>	<u>Av. % HF</u>	<u>Av. Temp. °C</u>	<u>Volts</u>	<u>Amps.</u>	<u>% Wt. Loss</u>
Low Brass	15.9	39.0	96	6	9.5	0.12
*Free Cutting Bras	16.3	40.2	105	6-9	10-4	0.25
Ampco 8	15.9	40.1	103	5.8	9.6	0.31
	16	39.7	101	6.2	10	0.32
Phos. Bronze	16.0	40.1	101	6.0	9.0	0.39
Everdur 1010	15.9	38.1	101	5.8	9.5	0.42
Commercial Bronze	16.0	41.9	100	6.0	9.5	0.45
Copper DHP	15.5	40.8	101	6.0	8.9	0.50
Magnesium	16.3	41.0	102	7.0	8.1	0.65
Monel	16.2	41.1	99	6.4	9.9	0.68
Steel 4140	16.0	40.4	102	6.0	8.4	0.70
Steel 1020	15.8	41.2	100	7.6	6.2	0.71
Stainless Steel 304	15.5	41.2	100	6.0	8.9	0.94
Stainless Steel 410	16.5	39.9	89	6.6	9.6	2.7
Hastelloy C	16.1	40.9	96	6.4	8.1	28.2

*Carbon anode swelled and broke during this run.

Table No. IV

MATERIALS LISTED ACCORDING TO DECREASING CORROSIVE RESISTANCE

<u>Current-Voltage Method</u>	<u>Constant Voltage Method</u>	<u>Pressure Plate Method</u>
Cartridge Brass	Free Cutting Brass	Low Brass
Free Cutting Brass	Cartridge Brass	Free Cutting Brass
Phos. Bronze*	Magnesium	Ampco 8
Be Copper	Copper ETP	Phos. Bronze*
Copper ETP	Copper DHP*	Everdur*
Ampco 8	Bearing Bronze	Commercial Bronze
Ampco 45	Tool Steel 10	Copper DHP*
Stainless Steel 410	Phos. Bronze*	Magnesium
Copper DHP*	Stainless Steel 410	Monel
Magnesium	Ampco 45	Steel 4140*
Ampco 83	Steel 1020	Steel 1020
Ampco 18	Ampco 18	Stainless Steel 304
Bearing Bronze	Be Copper	Stainless Steel 410
Steel 1020	Ampco 8	Hastelloy C
Tool Steel 11	Steel 1095	
Steel 1095	Ampco 83	
Everdur*	Everdur*	
Tool Steel 10	Silver Plate	
Steel 4140*	Stainless Steel 304	
Stainless Steel 304	Steel 4140*	
Monel	Cast Iron	
Cast Iron	Monel	
Lead		
Aluminum		

*Note that pressure plate is not in the same temper conditions as the rods. See Table V.

Table V
NOMINAL COMPOSITION AND CONDITION OF SAMPLES

Material	Trade Name Or Source	Al	C	Cr	Cu	Fe	Mg	Mn	Mo	Ni	P	Pb	Si	Sn	W	Zn	Other	Rockwell Hardness	Condition ⁽¹⁾	Yield psi	Tensile psi
Aluminum 24S		Bal			4.5		1.5	0.6										B73	T4	42,000	64,000
Cartridge Brass					70											30		F80	$\frac{1}{4}$ H	20,000	49,000
Free Cutting Brass					61.5							3.25				35.25		B77	H	42,000	58,000
Low Brass					80											20		F73	A	16,000	43,000
Bearing Bronze					83							7		7		3		F66	C	14,000	30,000
Commercial Bronze					90											10		B61	H	40,000	60,000
Phosphor Bronze	Anaconda A-351				94.75						0.25			5				B79 ⁽²⁾	$\frac{1}{2}$ H	55,000	70,000
Silicon Bronze	Everdur 1010				95.8			1.1					3.1					B85 ⁽³⁾	H	55,000	85,000
Beryllium Copper					98												2 Be	B91	$\frac{1}{4}$ H		88,000
Cast Iron			3.5			Bal		0.8					2					B85	C		40,000
Copper	DHP				99.9						0.04							F75 ⁽⁴⁾	10%D	32,000	40,000
Copper	ETP				99.92													F80	10%D	32,000	40,000
Hastelloy	C			16		6.5			17	Bal					4			B98	A	58,000	130,000
Lead												99.9 ⁽¹⁾							C		
Magnesium	Dow FS-1	3					Bal	0.2								1		F45		20,000	33,000
Monel					30					67								B85	$\frac{1}{2}$ H	63,000	84,000
Steel 1020			0.2			Bal		0.45										B89	900°D	67,000	93,000
Steel 1095			0.95			Bal		0.45										B92	A	52,000	98,000
Steel 4140			0.40	0.95		Bal		0.90	0.20									C32 ⁽⁵⁾	800°D	195,000	210,000
Stainless Steel 304				19		Bal		2		9								B98	CR	70,000	120,000
Stainless Steel 410				12		Bal		1										B92	CR	60,000	90,000
Tool Steel 10			1	0.5		Bal		1.2							0.5			B87	A		
Tool Steel 11			1			Bal		.3									0.2V	B80 ⁽⁶⁾	A		
Ampco 8		7			Bal	2.25												B91		40,000	80,000
Ampco 18		10.5			Bal	3.5												C27		47,000	95,000
Ampco 45		10.5			Bal	2.75				5.0								C21		68,000	110,000

(1) Approximate

(4) Pressure Plate F66 $\frac{1}{4}$ Hard

(2) Pressure Plate B97 Hard

(5) Pressure Plate B85 Annealed

(3) Pressure Plate B51 $\frac{1}{2}$ Hard(6) Pressure Plate B78 $\frac{1}{2}$ Hard

H=Hard, A=Annealed, C=Cast, D=Drawn, CR=Cold Rolled or Drawn

Figure II

CONDITION OF SAMPLES AFTER HIGH VOLTAGE TEST