PREFERRED RELIABILITY PRACTICES

SELECTION OF COMPATIBLE MATERIALS FOR USE WITH FLUORINE

Guideline:

Use established design guidelines for selection of materials that provide safe operation when exposed to elemental fluorine and fluorine-oxygen (FLOX) mixtures.

Benefit:

The design data provides a list of materials and conditions which are compatible for use with fluorine. The use of this data by design engineers will result in the selection of materials for use with fluorine that can provide safe and reliable system operation.

Center to Contact for More Information:

Lewis Research Center (LeRC)

Implementation Method:

Generally failures in systems using fluorine are caused by: (1) improper choice of materials and/or system components; (2) improper fabrication and assembly practices, (ref 1); and (3) improper system preparation and operating procedures, resulting in the presence of contaminants. This guideline applies design considerations to preclude failures caused by improper choice of materials. Design guidelines to address failure causes (2) and (3) are beyond the scope of this document (see Reference 1).

The design considerations to be used in selection of materials for use in fluorine systems should consist of:

a)[1] Selection of materials based on property requirements for the application (e.g., strength, thermal properties, welding or brazing characteristics, etc).

b) Selection of materials that can be fabricated without introducing contaminants and/or entrapped voids.

c) Consideration of effects peculiar to a fluorine environment (e.g., ignition temperature of material in fluorine, fluoride films and exposure to friction, moisture presence and compatibility with hydrogen fluoride, etc).

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[1]Design consideration (a) represents standard design approach and is presented here for completeness only.

The design considerations of (b) and (c) above are based on extensive

test experience from liquid fluorine rocket testing conducted at LeRC, and from materials tests conducted at LeRC and other laboratories.

References 1, 2, and 3 present material compatibility with liquid fluorine for metallic and nonmetallic materials, respectively. Table 1 below, extracted from reference 1 and presented here for purposes of illustration, lists the ignition temperatures and ignition delays for metals in fluorine.

Table 1. Ignition Temperatures of Metals in Fluorine
(a) Technique A

Metal	Wire diameter, in.	Ignition temperature, °C	Average ignition temperature, °C	Max variation from average, percent
Aluminum	0.010 0.016	----	(a)	---
Copper	0.0123	645 to 747	692	8.0
Iron	0.014	667 to 677	672	0.8
Molybdenum	0.0149	188 to 220	205	8.3
Monel	0.010	348 to 437	396	12.0
Nickel	0.008 0.0155 0.0154 0.0152	1168 1096 1219 1084	1162	6.0
Stainless Steel 302	0.020	570 to 796	681	13.0
Tungsten	0.0153	260 to 332	283	18.0

[a] An average of four tests gave an ignition temperature greater than the melting point.

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Table 1. Ignition temperature of Metals in Fluorine-Concluded
(a) Technique B

Metal	Wire diameter,(in)	Max wire temperature °C	Ignition delay, sec	Ignition temp range °C	Activation energy, kcal/mole
Copper	0.012	905 852 810 767 701 689	0.8 1.0 0.6 0.8 1.2 No ignition	689 to 701	39.5
Iron	0.014	730 676 648 644 618	1.0 1.6 2.0 2.2 No ignition	618 to 644	16.3
Nickel	0.015	1357 1306 1266 1253	0.6 1.2 0.6 No ignition	1253 to 1266	---

The data for Table 1 was obtained from tests using two techniques, techniques A and B. In technique A, an evacuated bomb was filled with gaseous fluorine at atmospheric pressure and the fluorine was increased in temperature by a heated wire. The temperature at which the wire burned is listed in the part of Table 1 for technique A. In technique B, the evacuated bomb was brought to temperature before fluorine introduction. The time required for the reaction to go to completion, the ignition delay, is listed in the part of Table 1 for technique B.

In addition, Table 2 was produced from Reference 1 which shows an expanded list of materials and their reactive effects with fluorine. Reference 1 also includes the effects of the presence of water and corrosion, the effects of fluoride films and their characteristics, and specific reaction of fluorine spills.

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Table 2. Compatibility of Materials in Fluorine

Aluminum and aluminum alloys	An aluminum trifluorine (AlF_3) film is formed on the surface of the surface of the metal or alloy. The melting point of aluminum is below its ignition point with fluorine gas.
Iron, iron alloys, steels	Ferrous and ferric films are formed at a higher rate and depth than other mild resistant metals. Reaction from moisture and hydrogen fluoride is also greater.
Stainless steels	Resistant to attack by hydrogen fluoride is greater than most mild steels. A fluoride film is formed with characteristics equivalent to Monel. The film becomes less stable at elevated temperature. Stainless steel welds behave similarly as the parent material.
Nickel (A, D, and L), Nickel bearing alloys, & Monel	Fluoride films are similar to that on aluminum, but are stable for use at high temperature (1200°F). Welding does not reduce the corrosion resistance of nickel or Monel if fluxes either are not used or are completely removed. Inconel, Illium, Illium "R", and Duranickel are less resistant than either nickel or Monel at higher temperatures but are generally similar to stainless steels.
Copper	Highly resistant to fluorine attack as are the copper alloys, red brass, and yellow brass. Cupric fluoride film is very stable in the presence of dry fluorine or dry hydrogen fluoride, but hydrolyzes readily in moisture to form hydrofluoric acid.
Titanium	Poor resistance to hydrogen fluoride. Liquid fluorine has the tendency to be highly reactive with titanium. Gaseous fluorine will attack titanium at temperatures above 300° F.
Silver solder: Nicrobraze	Recommended for most of the joining where welding is impractical or impossible. Connections made with this material have been highly reliable.
Chromium	Four fluorides are formed: 1) divalent, 2) trivalent, 3) tetravalent, and 4) pentavalent (3 an 4 are volatile). When chromium is reacted with fluorine below 300° F it forms a protective divalent fluoride film. Above 300° F, the fluoride is converted from a divalent to a volatile tetravalent fluoride form and loses its protective ability.
Beryllium	Behaves much the same way as nickel in fluoride film formation. Tantalum should not be used at temperatures above 150° F
Lead	Forms a nontenacious fluoride film. In passive exposure it has been used successfully as a seal or gasket material.
Tin	Reacts similarly to lead and can also be used for soft gaskets in cryogenic service.
Rhodium, palladium, platinum	Can be used on contact with fluorine at room temperature generally without attack. These metals are used in some equipment because they are inert to hydrogen fluoride.

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The list in the above table shows a variety of metals which are compatible to a certain degree in fluorine. Generally nonmetallic materials are incompatible with fluorine, with the exception of ruby and Teflon (see References 1 & 3). It should be understood by the designer that material selection is dependent on the environmental conditions. To assist the designer in developing a safe fluorine system, Table 3 lists recommended materials to be used under certain operating conditions.

Table 3. Recommended Materials for High and Low Pressure Operations

HIGH AND ATMOSPHERIC PRESSURE OPERATIONS	
Materials Preferred	
High Pressure: (>14.7-1500 psi.) Nickel or Monel	More resistant to ignition than steel. These metals are preferred when handling pure fluorine under pressure. Monel piping can even be used at higher pressures than Nickel.
Atmospheric Pressure: Copper, Iron, Stainless Steel, and Brass	If the piping wall thickness is adequate, i.e., as in standard or extra-strong pipe, the material weight and surface area are large enough to eliminate spontaneous combustion.
High & Low Pressure Connections: Welding, Flange joints	Through experiments, welding has proved to be highly reliable in high and low pressure. Soft solder and fluxes should not be used, however. Flange joints are preferred when necessary, gaskets must be limited to soft metals, lead, tin, copper or aluminum.
Valves	Bellows-sealed valves generally can be used up to 100 psi., in 1-inch and larger sizes. The Hoke Monel needle valves or the Kerotest 440-A packed with Teflon or its equivalent have been successful. Metal-seated valves with Monel or aluminum-bronze seat-and-disk combinations have also been used successfully for low pressure valves.

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Technical Rationale:

Certain effects peculiar to a fluorine environment need to be considered by the designer. Fluorine is a highly reactive oxidizing agent; it has the highest oxidation potential of all elements. Fluorine can react with practically all organic and inorganic substances with few exceptions. Exceptions include the inert gases, fluorinated compounds in their highest state of oxidization, and a few fluorinated polymers.

Whether a substance will burn spontaneously in fluorine, or whether fluorine will replace an oxidant having a lower oxidizing potential, depends on the following conditions of exposure, (Reference 1):

1. Initial temperature of the region.
   Reaction is initiated by reaching the ignition temperature or by providing activation energy from impact, friction, high flow, or reaction of contaminants.

2. Initial pressure of the region.
   It has been found that ignition temperatures are lowered by increasing pressure.

3. Thermal conductivity if the material is a solid.
   Combustion will not occur if heat of reaction can be removed by conduction and the temperature can be maintained below ignition temperature of material.

4. Exposed surface area with respect to mass of the substance.
   Generally, surface reactions with most metals will form a fluoride film and inhibit further reaction. Large exposed surface-area-to-mass material forms (fine mesh screen, powered metal, etc.) can have surface reactions that are highly reactive and can increase temperatures to initiate combustion.

5. Kinetic or static exposure.
   It has been found that kinetic energy from flow dynamics can contribute to activation energy for combustion.

6. Fluorine concentration in the region.
   Reactivity increases with increased fluorine content of liquid or gaseous mixtures.

Fluorine can react combustively with water depending on the size of water droplets. Ice will react combustively with liquid fluorine. In the presence of water, the fluorine will react to form hydrogen fluoride potentially resulting in corrosion. Therefore, the entry of water into the system in any form, even from non-dry purge gases or moisture laden air, is to be avoided.

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In addition to the selection of materials based on property requirements for the application (i.e. strength, thermal properties, welding or brazing characteristics, etc), the selection of materials for use with fluorine must consider the introduction of contaminants into the system and whether a given material will burn spontaneously in the presence of fluorine. Materials selected must be cleaned free of contaminants and fabricated without introducing contaminants and/or entrapped voids. The contaminant can be in the form of a material additive or foreign material (ice, moisture, grease, soil, etc.) which unintentionally enters the system. The contaminant can then react with fluorine and cause local temperatures to exceed the ignition temperature for that part of the system, resulting in failure. The presence of voids can lead to trapped contaminants that escape cleaning procedures and therefore must be avoided.

Impact of Nonpractice:

Failure to use the design data presented in this guideline will result in unsafe systems and failures which are costly and potentially injurious to personnel and environment.

References:

1. Schmidt, H. W.: "Fluorine and Fluorine-Oxygen Mixtures in Rocket Systems," NASA SP-3037, 1967.

2. Schmidt, H. W.: "Compatibility of Metals With Liquid Fluorine At High Pressures and Flow Velocities," NACA RM E58D11, 1958.

3. Price Jr., H. G. and Douglass, H. W.: "Nonmetallic Material Compatibility With Liquid Fluorine," NACA RM E57G18, 1957.

4. Slesser, Ph.D. Charles and Schram, Stuart R.: "Preparation, Properties, and Technology of Fluorine and Organic Fluoro Compounds," McGraw-Hill, New York, 1951.