Fig. 13 Schematic of simple tank pressurization system.

use a liquid expulsion system in which the liquid flow rates are variable, but it is desirable to have the driving pressure remain reasonably constant.

Conclusions

The vortex valve has proven to be a suitable valving element for throttling the flow of hot gas from a typical high-performance solid propellant. The flow of 5500°F 16% aluminized from a gas has been throttled from 1 lb/sec to complete shutoff. The valve design has an operational life of 50 sec without serious material degradation. Possible applications of the vortex valve are: secondary injection thrust vector control, engine thrust control, thrust termination, and tank pressurization.

References

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Compatibility of Materials with Chlorine Pentafluoride

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Thirty-four materials (aluminum, copper, iron, and nickel alloys and plastics) were static tested for compatibility with ClF$_5$ and with moisture contaminated ClF$_5$ at ambient temperatures and at 160°F for 30 days; tests also were conducted for 580 days at ambient temperature. Results of visual and metallographic examinations and weight changes are reported. General corrosion in uncontaminated ClF$_5$ was small for all alloys tested. General corrosion was well within normally acceptable corrosion limits (2 mil/yr) for all alloys tested. Optical microscopy showed that severe localized attack of second phases or inclusions (stringers) occurred in the following monel alloys: 400, R-405, 500, 501, and 507. There was no noticeable surface attack of the nonmetallic materials, but these materials did gain considerable weight due to absorption to ClF$_5$. The alloys most resistant to attack by ClF$_5$ under all test conditions were Hastelloy C, Nickel 210, René 41, and Inconel X-750.

Introduction

CHLORINE pentafluoride (ClF$_5$) is a recently developed, dense, stable, storable oxidizer with a wide liquid temperature range. Its properties are remarkably similar to those of ClF$_3$, but it has superior rocket engine performance capabilities, and, in fact, is the most powerful, storable liquid oxidizer. A variety of physical and engineering properties of importance to rocket engine usage was determined under Air Force Contract AF04(611)-9563, including an evaluation of the compatibility of 34 engineering materials with ClF$_5$ under static conditions. The selection of the materials was based on utilization in the aerospace industry. The tests were conducted under conditions that simulated, as closely as possible, actual propellant storage conditions. Tests were conducted with high-purity (closed-system loaded) ClF$_5$ under ambient temperature (T_a) conditions (40°–100°F) and under controlled high-temperature conditions (160°F). In addition, selected materials were tested with moisture-contaminated ClF$_5$; i.e., the ClF$_5$ was loaded in the test chamber in the open air. The results of the compatibility investigation are presented herein.

Experimental Procedure

The test apparatus (Fig. 1) was made up of a 10-in.-long, 1-in.-diam, stainless-steel tube with a stainless-steel bellows valve at the top and a stainless-steel plug at the bottom. The tube was lined with Kel-F sheet to prevent galvanic corrosion between the samples and the stainless-steel wall of the bomb. A group of specimens was suspended on a Teflon-coated wire with alternate Teflon spacers. Each specimen was isolated from other specimens, below and above, by alternating Kel-F disks (Fig. 2) to avoid contamination from one specimen to another. This setup provided a means

Table 1　Materials compatibility samples

Material	Heat treatment or condition	Material	Heat treatment or condition
Group 1		Group 2	
1100 Al	0	Inconel X-750	$\sigma_{tu} = 150$ ksi
2024 Al	T3	304 SS	Full hard
2024 Al	T351	316 SS	Full hard
2219 Al	T351	347 SS	Full hard
6061 Al	T651	René 41	1950°F, 1 hr, air cooled
6066 Al	T6		1400°F, 16 hr, air cooled
7075 Al	T6	Hastelloy C	Solution heat-treated
7079 Al	T651	Nickel 200	Annealed
5457 Al	0	Nickel 211	Annealed
X7002 Al	0	Kel-F 81	
5096 Al	0	Group 4	
Group 3		Monel 400	Annealed
410 SS	$\sigma_{tu} = 180$ ksi	Monel 402	Annealed
PH 15-7 Mo	Rh1050	Monel K-500	Aged
AM 350	SCT 850	Monel 501	Aged
AM 355	SCT 1000	Monel R-405	Annealed
FEP Teflon		Monel 505	Annealed
TFE Teflon		ETP Copper	Hard

for segregating and collecting corrosion products for future analysis and evaluation. When loaded, the bombs were suspended vertically to insure a horizontal orientation of the specimens and Kel-F disks.

For the closed-system loading of ClF₅, each bomb was first passivated with ClF₅ vapor to 25 psig. The bomb was then

Table 2　Visual examination of specimens exposed to uncontaminated ClF₅[a]

Material	30-day, T_a test	30-day, 160°F test	580-day, T_a test
Monel 400	NC	S dull	DD, dark spots
Monel 402	NC	NC	DD
Monel K-500	NC	DD	DD
Monels 501 and R-405	NC	DD	DD, dark spots
Nickel 200	NC	NC	S dull
Nickel 211	NC	NC	DD
Monel 505	NC	P, D	DD, dark spots
Inconel X-750	NC	NC	DD
Monel 507	NC	P, D	P, DD
Hastelloy C	NC	NC	NC visible
AM 355	SD	Olive-colored film	NC
AM 350	NC	Green film	NC
1100 Al[b]	NC	Dull	NC
PH 15-7 Mo	Yellowed	Dull yellow	NC
X7002 Al	S dull	NC	NC
5457 Al	NC	NC	NC
7075 Al	SD	NC	NC
304 SS	SD	NC	NC
316 SS	SP	NC	NC
347 SS	SP	NC	NC
410 SS	NC	Dull film	NC
René 41	SD	Semidull	SD
2219 Al	NC	NC	NC
6066 Al	SP	NC	NC
ETP copper	NC	Dull	Dull
TFE and FEP Teflons	Softened	Softened	Black discoloration around perimeter
Kel-F 81	NC	NC	NC visible

[a] NC = no change; D = discolored; DD = dull, discolored; P = pitted; S = slightly.
[b] Aluminums 6061, 5086, 7079, 2024 (T3), and 2024 (T351) showed no change in all 3 tests.

Fig. 1　Compatibility bomb with suspended sample disks.

loaded with 47 cm³ liquid which was half the total volume. This arrangement insured that half the specimens would be exposed to liquid and the other half to vapor. A closed system loading technique was used to prevent air contamination of the ClF₅. In a preliminary, 30-day compatibility test at a controlled temperature of 86° ± 2°F, solid-Teflon sample bombs for each material were loaded with ClF₅ in a direct, open-air transfer. This test was used to evaluate the effect of handling ClF₅, under open conditions. The ClF₅ was obviously contaminated with air and moisture that had condensed on the prechilled bomb walls.

The materials for this program were divided into four groups, which are listed in Table 1 along with the heat treatments or conditions for each material. Group 1 comprised various aluminum alloys; Group 2, nickel-base alloys, austenitic stainless steels, and Kel-F 81; Group 3, martensitic stainless steels and two Teflon materials. Monel alloys and ETP copper comprised the fourth group. Each group of materials was loaded in a separate bomb with materials from each group in both the vapor and liquid phase. This separation of materials into groups was intended to eliminate erroneous results due to contamination and interaction between sample groups.

A set of four bombs (one for each of the specimens) made up a system for testing. One system was tested for 30 days at ambient temperature ($T_a = 40°-100°F$); two systems were tested for 580 days at T_a; and one system was tested for 30 days at 160°F. A special test was conducted that consisted of a 30-day test at T_a in moisture-contaminated ClF₅, using a separate solid Teflon bomb to contain each material with two specimens each in liquid and vapor. After the tests were conducted on each set, the specimens were removed from the bombs and analyzed. To prevent contamination by moisture from the air, the specimens were removed from the ClF₅ atmosphere in a dry-nitrogen atmosphere.

Specimens were analyzed visually, by weight gain or loss, and finally, metallographically. Metallographic analysis inherently offers the most exact method of studying contamination in a program of this nature, but, because of the expense involved, only a selected group of exposed specimens were examined metallographically. While weight change is the classic method for determining compatibility, the probability of errors resulting from fluorides flaking off and/or moisture contamination is very high. Also, localized attack cannot be evaluated by weight change. Ideally, metallographic examination should be the basis of an evaluation with weight change used in association with it.

Results

Visual Examination

All specimens were examined visually when the tests were completed (Table 2). After the surfaces of the specimens were purged and dried, they showed no change in appearance when exposed to room temperature except for the copper
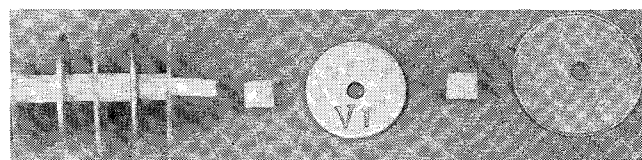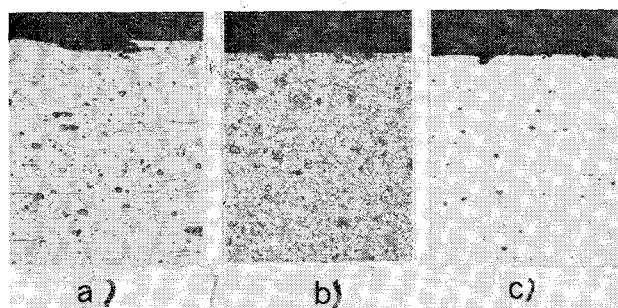

Fig. 2　Suspension of sample disks.

Fig. 3 Exposed to uncontaminated ClF₅ for 30 days at T_a, magnification 250×, Keller's etch [a) Al × 7002-T6, b) Al 7079-T6, c) Al 7075-T6].

specimen, which turned green on air exposure. Specimens were generally much less affected by exposures to uncontaminated ClF₅, both liquid and vapor, than to air- or moisture-contaminated ClF₅. The aluminum alloys showed no corrosion pitting, and the specimens had the same bright appearance as before testing. Some dulling of appearance was noted after the specimens had been exposed to air for several days after exposure to ClF₅. The austenitic stainless-steels showed a slight amount of pitting and discoloration after 30 days (T_a) testing. Interestingly, there was no change in appearance after 580 days testing. This may be due to slight variation in the two test setups. There was also no change in appearance after the 30-day 160°F test. The nonaustenitic stainless-steel specimens were discolored and dull, with a slight surface attack noticeable at spots on the AM 350 and AM 355 specimens after the 580-day test. The discoloration and film formation were greater with increasing temperature. All samples had a thin film, but the film was heavier on the 410 stainless-steel specimens. Nickel 211 and Nickel 200 showed no visible change after 30 days in ClF₅ at T_a and 160°F. They were dull and discolored after the 580-day test. Hastelloy C showed no visible change under any of the test conditions. René 41 was slightly discolored after T_a tests, and had a dull film after the 160°F test. Inconel X-750 showed reaction only after the long-duration test. A comparison of the results for the nickel-base alloys showed similarities between the results of the 30-day 160°F and the 580-day T_a tests but very little agreement with the results of the 30-day T_a test. It should be noted that the same type of agreement occurred within the austenitic steels and that the nickel-base and austenitic stainless-steel specimens occupied the same container during each of the tests. The copper and monel alloys showed no visual change after the 30-day T_a test and were slightly discolored and dull after the 160°F test. Monel surfaces were discolored and dull after the 580-day exposure and the two cast monels (505 and 507) showed some pitting in the areas where the numbers were stamped. No attack was visible on the surface of the ETP copper. A slight general dulling of the surface occurred. No visible attack was noticeable on any
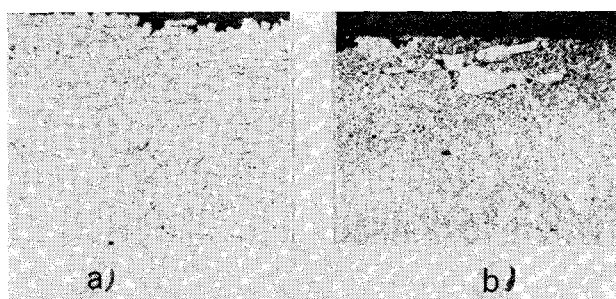

Fig. 4 Exposed to uncontaminated ClF₅ for 30 days at T_a, magnification 250×, ammonium sulfate etch [a) AM 350, SCT 850 condition, b) AM 355, SCT 1000 condition].

Table 3 Weight change or alloys exposed to ClF₅ under various conditions

| | Material weight change, 10^{-2} g/m² | | | | | |
| | Liquid-exposed samples | | | Vapor-exposed samples | | |
Material	30 days at T_a	30 days 160°F	580 days at T_a	30 days at T_a	30 days 160°F	580 days at T_a
Aluminum alloys						
1100	+19	+157	−73 −129	+19	+195	0 −165
2024 (T3)	−57	+98	−190 −153	−57	+118	−76 −172
2024 (T351)	−95	+78	−76 −192	−38	−97	0 −173
2219 (T351)	−55	+78	−75 −166	−55	+118	−243 −186
5086	0	+118	−56 −166	0	+39	−74 −167
5457	−38	+98	−95 −133	−57	+137	−95 −152
6061 (T651)	−92	+118	−74 −166	−19	+137	−74 −147
6066 (T6)	−75	+157	−19 −187	−19	+137	−112 −149
X7002	+38	+78	−95 −94	+38	+98	−75 −152
7075 (T6)	+38	+78	−95 −152	+57	+59	−115 −112
7079 (T651)	+19	+118	−74 −167	+56	+137	−37 −167
Stainless steels						
Austenitic						
304	+224	+78	0 +57	+150	+78	−19 +38
316	+246	+98	+57 +19	+471	+59	+57
347	+228	+118	0 +57	+265	+137	−19 +19
Nonaustenitic						
PH 15-7 Mo	+395	+157	+20 +56	+152	+118	0 0
AM 350	+77	+118	+58 0	−77	+177	+19 −19
AM 355	+176	+236	+257 +237	+117	+372	+277 +158
410	+206	+609	+627 +568	+94	+411	+701 +625
Nickel-base alloys						
Nickel 200	+225	−98	0 +19	+246	−78	−19 0
Nickel 211	+323	+20	+19 +38	+208	0	−19 −20
Inconel X-750	+374	0	−20 +40	+376	0	−20 +39
René 41	+304	+118	+37 +37	+238	+137	+57 +38
Hastelloy C	+215	+20	+39	+273	0	−58 −916
Copper or monel alloys						
Monel 400	+406	+39	+58 +58	+410	+59	+116 +39
Monel 402	+303	−39	+117 +77	+252	−20	+19 +76
Monel R-405	+350	+98	+377 +77	+402	+59	+377 +77
Monel K-500	+309	+39	−19 +19	+309	+39	+77 −19
Monel 501	+615	+236	+231 +192	+575	+59	+270 +173
Monel 505	+299	−489	+99 +20	+358	0	+141 +20
Monel 507	+457	+570	+201 +120	+422	+471	+300 +161
ETP Copper	+332	+32	+135 +39	+272	+118	+214 +39
FEP Teflon	...	+1119	+3464	...	+1059	+3475
TFE Teflon	...	+510	+1973	...	+489	+1702
Kel-F 81	...	...	+7282 +7450	...	...	+4912 +7115

of the nonmetallic specimens except the 580-day test, and then the only change visible was a black discoloration around the edge.

Weight Change

Weight changes per unit area (10^{-2} g/m²) after exposure to uncontaminated ClF₅ under the different test conditions are presented in Table 3. For aluminum alloys, after 30 days, four of the T_a samples and all of the 160°F samples had weight gains (indication of passivation) instead of weight

Table 4   Film formation rates (mil/yr) for 30-day exposure at ambient temperature to air- and water-contaminated ClF₅ and uncontaminated ClF₅
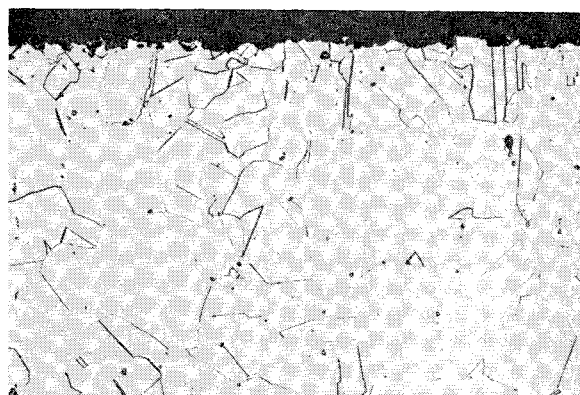
Alloy	Contaminated ClF₅		Uncontaminated ClF₅	
	Vapor	Liquid	Vapor	Liquid
AM 350	0.2	...	0.1	0.1
AM 355	0.2	...	0.1	0.1
Nickel 200	0.2	0.2	0.1	0.1
Nickel 210	0.1	0.1	0.1	0.2
Monel 400	0.7	0.1	0.2	0.2
Monel 402	0.5	...	0.1	0.2
Monel R-405	0.2	...	0.2	0.2
Monel K-500	0.7	...	0.3	0.2
Monel 501	0.8	...	0.3	0.4
Monel 505	0.5	...	0.2	0.2
Monel 507	0.6	...	0.2	0.3
Inconel X-750	0.3	0.3	0.33	0.3
Hastelloy C	0.1	0.1	0.1	0.2
Electrolytic tough Pitch (ETP)	0.2	0.4	0.15	0.2

Fig. 5   Exposed to moisture-contaminated ClF₅ for 30 days at T_a, magnification 200× [Nickel 211 (D nickel)].

losses. After the 580-day tests, aluminum alloy specimens had lost weight in both the liquid and vapor. The magnitudes of the weight losses were similar for all alloys and well within the corrosion resistance rating level (<2 mil/yr) established as exceptable by the Defense Metals Information Center. For the austenitic stainless steels, the weight gains resulting from the 580-day, T_a tests were comparable to those for the 30-day, 160°F tests and slightly less than those for the 30-day, T_a tests. The 300-series stainless steel, liquid-exposed samples had very small weight gains. There were slight weight losses for two of the samples exposed to the vapor for 580 days. The remainder of the vapor-exposed samples had slight weight gains. The nonaustenitic stainless-steel results were similar for each of these materials over the various test conditions except for the 15-7 Mo PH specimen, which exhibited less change during the long-term tests than in the shorter tests. After the 580-day exposures, the 15-7 Mo and AM 350 samples showed slight weight gains, while the AM 355 and 410 stainless steels had larger weight gains. The nickel and nickel-base alloys showed some similarities between the results for the 30-day, 160°F tests and those for the 580-day, T_a tests, but little or no agreement with the 30-day, T_a tests. The 30-day, T_a test results showed significantly greater weight gains than the other two test conditions. The liquid-exposed 580-day and 30-day, 160°F specimens showed small weight gains; however, generally, the vapor-exposed samples experienced small weight losses. With few exceptions, copper and the monel alloys experienced slight-to-moderate weight gains; the gains for the 30-day, T_a tests were generally larger than those found for the 580-day, T_a and 30-day, 160°F tests. Long-term testing of the nonmetallics resulted in weight gains as expected from testing at 160°F in a previous program; they absorbed small amounts of ClF₅, with the amount absorbed varying as follows: Kel-F 81 > FEB Teflon > TFE Teflon.

The results of tests in moisture-contaminated ClF₅ for 30 days at T_a are compared with results for exposure to uncontaminated ClF₅ in Table 4. The small amount of water caused the rate of film formation to double, except for the Nickel 210, Hastelloy C, Monel R-405, and Inconel X-750 alloys.

## Metallographic Findings after 30-Day, T_a Exposures

Metallographic pictures of exposed aluminum alloys are shown in Fig. 3. Alloy X7002-T6 suffered a slight amount of "wormhole" attack extending 0.002 in. in from the surface after exposure to uncontaminated ClF₅ vapor at T_a for 30

days. 7079-T6 aluminum alloy showed a very bright surface layer after the same exposure, and 7075-T6 suffered a very slight general attack. Aluminum alloys 6066-T6, 2219-T6, and 2014-T35 were not visibly attacked under the same conditions. Figure 4 shows the corrosion damage to stainless-steel samples. The AM 350 alloy, in the subzero-cooled and 850°F aged condition, was affected slightly by exposure to moisture-contaminated liquid ClF₅ at T_a for 30 days. The attack appeared to be a general fingering type with no apparent preference for the second-phase precipitate. AM 355 alloy, in the sub-zero-cooled and 1000°F condition, showed a slight attack, possibly associated with a massive, light etching phase. Type 316 austenitic stainless steel had no attack from exposure to uncontaminated liquid ClF₅.

No attack was observed on the Nickel 200 (A Nickel) exposed to moisture-contaminated liquid ClF₅ at T_a for 30 days. Nickel 211 (D Nickel), which contains manganese, formed a surface reaction film in the same environment to a thickness of 0.005 in. (Fig. 5). Results obtained from testing Inconel X-750 specimens were inclusive, because the original specimens were descaled by a treatment that caused intergranular corrosion. The extent of the intergranular corrosion did not appear to increase with ClF₅ exposure. The René 41 alloys exposed to liquid ClF₅ at T_a for 30 days showed no attack. Although Hastelloy C is a nickel-base alloy, it did not react like the other nickel-base alloys. In the unaged condition, it appeared to be more resistant to ClF₅ than any other alloy tested. No attack was present. The metallographic study of copper and the various monel alloys revealed no cases of intergranular corrosion, either in dry or moisture-contaminated ClF₅. The most obvious metallographic result concerned the high-silicon, free-machining cast monel (Monel 507). Massive attack of silicon-rich areas by the moisture-contaminated liquid ClF₅ was observed (Fig. 6). The cast high-silicon monel without precipitated[5] graphite, M Monel 505 (S-Monel), did not undergo such massive attack, although a wormhole attack was noted
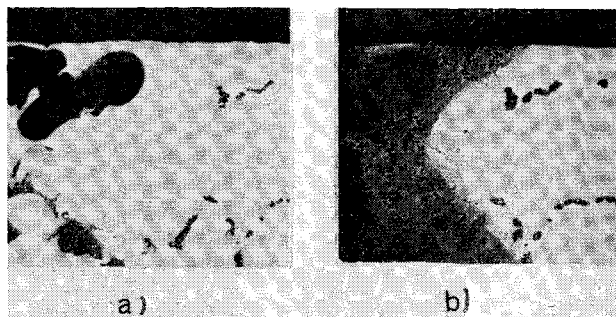
Fig. 6   Monel 507 exposed to moisture-contaminated ClF₅ for 30 days at T_a, magnification 250 ×[a) Unetched, b) Carapella's etch].
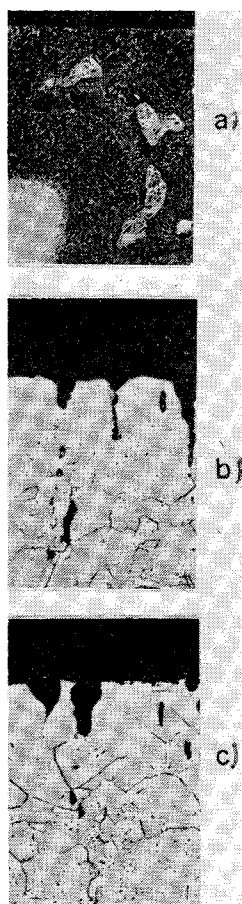
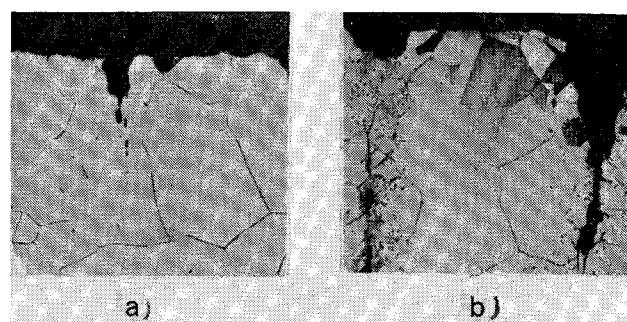Fig. 7   Exposed for 30 days at T_a magnification 200×, Carapella's etch [a) Monel 505 (S-monel) moisture-contaminated ClF₅, b) Monel 501 (kR-monel) moisture-contaminated ClF₅, c) Monel 510 (kR monel) uncontaminated ClF₅].

(Fig. 7). The wrought, age-hardenable, free-machining Monel 501 (KR-Monel), suffered deep, narrow attack associated with inclusion stringers in both the moisture-contaminated and uncontaminated ClF₅. The wrought, age-hardenable monel without precipitated graphite, Monel 500 (K-Monel), showed a resistance to metallographic etching on the surface exposed to ClF₅. A blocky attack possibly due to grain dropout was also apparent in the K-Monel exposed to both moisture-contaminated and uncontaminated ClF₅ (Fig. 8). The wrought monel with sulfur added to improve machining, Monel R-405 (R-Monel), suffered attack associated with stringers even in uncontaminated ClF₅ vapor. The attack on R-Monel was more severe in moisture-contaminated vapor. Monel 402, a wrought alloy developed for resistance to H₂SO₄, was not subject to severe localized attack even in moisture-contaminated ClF₅ liquid, but a slight localized attack was visible. Uncontaminated ClF₅ vapor did not attack this alloy. Monel 400 appeared to have a considerable number of stringers. Attack was related to these stringers even in the uncontaminated ClF₅ vapor. These results are
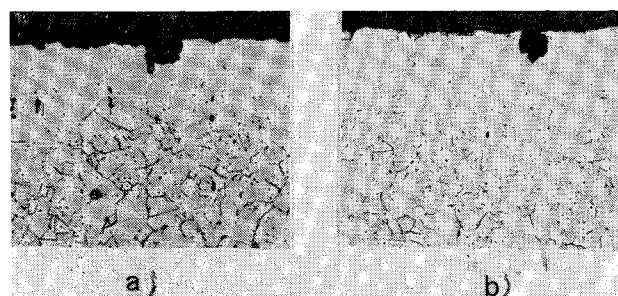
Fig. 8   Monel 500 (K-Monel) exposed for 30 days at T_a, magnification 200×, Carapella's etch [a) moisture contaminated ClF₅, b) uncontaminated ClF₅].

Fig. 9   Monel 405 (R-Monel) exposed for 30 days at T_a, magnification 250×, Carapella's etch [a) Uncontaminated ClF₅, b) Moisture-contaminated ClF₅].

shown in Figs. 9 and 10. Electrolytic tough pitch copper suffered a slight uniform surface attack in moisture-contaminated ClF₅ liquid. Copper exposed to uncontaminated ClF₅ vapor at room temperature suffered somewhat less attack (Fig. 11).

Metallographic Findings after 30-Day, 160°F Exposures

No attack was observed on 2024-T351 aluminum exposed to uncontaminated ClF₅ liquid at 160°F for 30 days. 7075-T6 and 7079-T6 aluminum alloys developed a surface reaction layer approximately 0.001-in. thick. Although the 7075 alloy had a copper-colored tinge on the surface under visual examination, the metallographic study did not show any evidence of this. Type 347 austenitic stainless steel was slightly attacked at the inclusions. These results are seen in Fig. 12. AM 350-SCT 850 developed a surface reaction layer less than 0.001 in. thick; Nickel 200 suffered a slight intergranular attack (Fig. 13). René 41 showed no attack. Hastelloy C appeared to be completely unaffected by the exposure. K-Monel alloy showed extensive attack of stringer inclusions. These results are shown in Fig. 14.

Discussion

Metallurgical examination showed that none of the primary phases of any of the materials tested were subject to severe attack by dry liquid or vapor ClF₅. However, attack occurred, sometimes severe, at certain inclusion and second phases in cast (silicon-rich) and free-machining monel exposed to moisture-contaminated ClF₅. Although there were wide variations in weight change and visual appearance be-
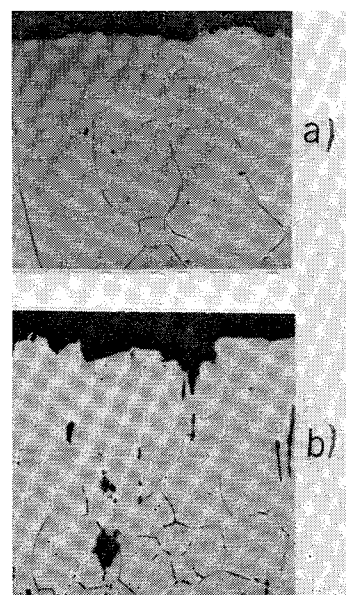
Fig. 10   Exposed for 30 days at T_a, magnification 250×, Carapella's etch [a) Monel 402, moisture-Contaminated ClF₅, b) Monel 400, uncontaminated ClF₅].

Table 5   Melting temperatures, free energies of formation, and volume ratios of metal fluorides

Fluoride	T_m, °F	$(\Delta E)_f$ 23°C, kcal/mole-°F	$V_m{}^a$ V_f
AlF	1521	−97	. . .
AlF₃	2359	−102	2.9
FeF₂	2016	−79	3.2
FeF₃	1881	−73	4.5
CrF₂	2016	−86	3.0
CrF₃	2012	−83	4.0
CrF₄	693	−67	. . .
CrF₅	212	−65	. . .
MoF₄	1035	−59	. . .
MoF₅	171	−63	. . .
MoF₆	79	−64	8.8
CbF₅	169	−64	6.1
NiF₂	1000	−73	3.2
Sublimates			
CuF	1175	−55	. . .
CuF₂	1701	−50	3.4

^{a} (Volume fluoride/mole)/(volume metal/mole).

tween the various samples, the resistances of all materials tested (to attack by ClF₅) would be placed in the excellent category (the weight changes were very small based on corrosion standards established by the Defense Metals Information Center). The results from the 30-day, 160°F and 580-day, T_a tests are more comparable than those from the T_a, 30-day and 580-day tests; i.e., small increases in temperature cause greater corrosion damage than large increases in time.

Among the metallic materials, only aluminum alloys showed definite weight losses, indicative of corrosion. However, there is visible evidence of corrosion in the monel and nonaustenitic stainless steel group. Weight gains indicative of passivation film formations were noted and observed for the other metals. However, in every case there was a loss of weight between 30 and 580 days (Table 3), which could be accounted for in the following manner. Since fluorine is more electronegative than chlorine and, in fact, has the highest oxidation potential of all elements, the compatibility of metals with ClF₅ is a problem of reaction of metals with fluorine. Fluorine will react with virtually all materials except the metal fluorides; reactivities for the pertinent metals are summarized in Table 5. The fluoride of Cr, Mo, Cb, and Ni are included in this table because these elements are alloying elements in the stainless steels. Most of the metals have several stable fluorides as indicated by their free energies of formation. Most of the fluorides have sufficiently high melting points to be solid during the tests, and if they are coherent, they will act as barriers to further reaction.
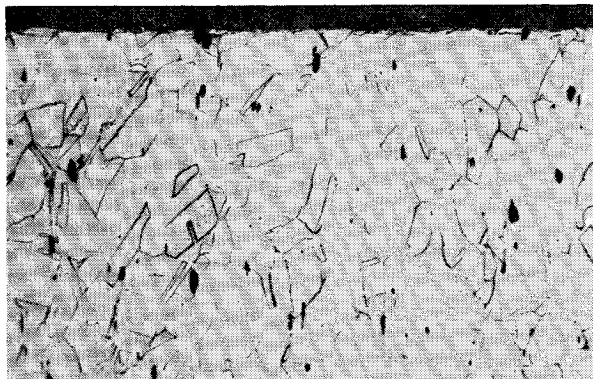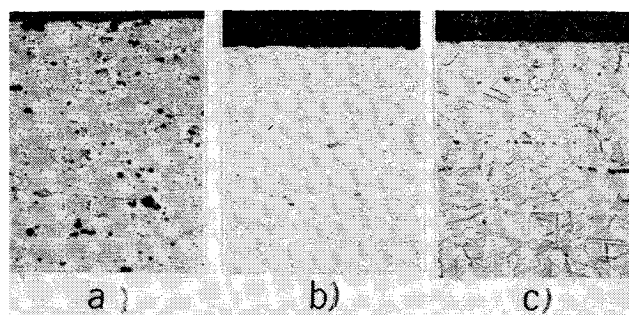
Fig. 12   Exposed to uncontaminated ClF₅ for 160 days at at 160 F, magnification 250× [a) Al 7075-T6, Keller's etch, b) 7079-T6, Keller's etch, c) 347 SS, chromic acid etch.]

The coherency of the fluoride on the metal substrate is mainly determined by the volume ratio between the fluoride and the substrate (V_f/V_m). Table 5 also lists for V_f/V_m each fluoride for which density is available. From volume ratios alone, aluminum would be predicted to be the least reactive with fluorine, followed by the copper-nickel alloys, and lastly by the stainless steels. The volume ratios for all of the fluorides are higher than would be predicted to give long-duration protection. For example, the aluminum and titanium metal oxide/metal volume ratios are between 1.4 and 2.0, and these metals have long-duration resistance to oxygen environments.

As the thickness of the fluoride layer increases, the propensity toward flaking, cracking, or even powdering of the fluoride increases. Thus, there is an increasing likelihood of losing fluoride coherency. Because the higher molecular weight fluorides have the highest volume ratios, only the surface fluorides would be likely to crack or be removed from the metal, leaving a coherent lower molecular weight fluoride next to the metal that would tend to continue metal protection. Therefore, this analysis suggests that initial exposure to fluorine results in weight increase due to coherent fluoride formation. As exposure continues, coherency with the higher molecular weight fluorides is lost, resulting in partial loss of the fluoride from the surface and eventual weight loss of the metal. Experimentally, most of the exposure showed that this occurred; i.e., initially there was a weight gain and then on long-duration exposure a weight loss.

The metallographic results showed that the nickel-base alloys, René 41, and Hastelloy C had the least attack of any of the metallic materials. Nickel 200 showed some slight fingering attack. Aluminum alloys were the next least affected. They suffered some slight surface attack only.
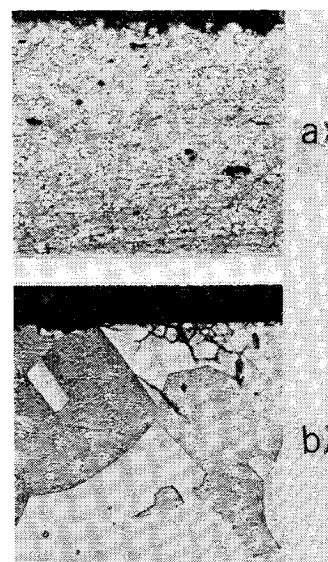
Fig. 13   Exposed to uncontaminated ClF₅ for 160 days at 160 F, magnification 250× [a) Am 350, SCT 850 condition, ammonium sulfate etch, b) Nickel 200 (A Nickel), chromic acid etch].
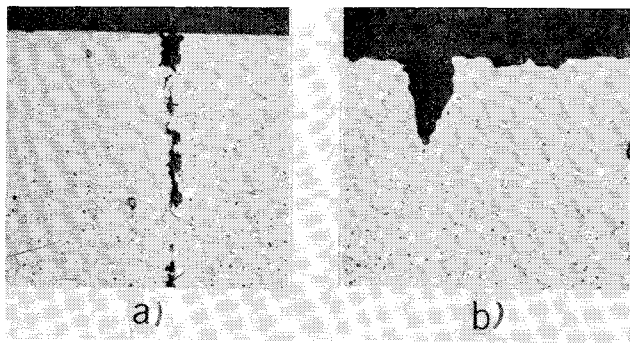

Fig 11   Exposed to uncontaminated ClF₅ vapor for 30 days at T_a, magnification 200× (electrolytic tough pitch copper).

Fig. 14 K-Monel exposed to uncontaminated ClF₅ for 30 days at 160 F. Attack associated with stringer inclusions [a) Magnification 100×, b) Magnification 250×].

Austenitic stainless steels were less affected by the ClF₅ environments than the precipitation-hardenable stainless steels, which showed a slight fingering attack at the surface. The cast monel alloys, as compared to the other materials, were attacked along the massive silicon-rich areas. The wrought alloys were not affected to the extent of the cast alloys. There was an attack along the stringers of the free-machining grade and some general attack that occurred in the K-Monel specimen. In general, it appears that the presence of large second-phase segregation in any material might pose a problem. This discussion is based only on metallographic examination of specimens exposed to ClF₅ for 30 days; 580-day exposures probably would have shown greater effects.

Teflon and Kel-F 81 plastics indicate that these materials are acceptable for use in static applications under the conditions of these tests; however, these materials absorb ClF₅ liquid and vapor, which might be somewhat troublesome.

The results of the 30-day tests in moisture-contaminated ClF₅ indicated that all of the materials tested were compatible. However, small amounts of moisture did double the rates of film formation. It is well known that moisture reacts with ClF₅ to form HF, which reacts more rapidly than

fluorine with the metal surface to give a thicker reaction layer in the moisture-contaminated ClF₅. Nickel 210, Inconel X-750, and Hastelloy C did not show increased film formation in the presence of moisture-contaminated ClF₅.

Conclusions

The following conclusions can be drawn from these tests of static exposure of unstressed specimens to ClF₅ for 30 days at T_a or 160°F, and 580 days at T_a:

1) General corrosion in uncontaminated ClF₅, as shown by visual examinations and weight change, was small by accepted corrosion standards for all alloys tested.

2) General corrosion in moisture-contaminated ClF₅ was usually considerably greater than in uncontaminated ClF₅ but was still well within normally acceptable corrosion limits (2 mil/yr) for all alloys tested.

3) The alloys most resistant to attack by ClF₅ under all test conditions were Hastelloy C. Nickel 210, René 41, and Inconel X-750.

4) Optical microscopy revealed that severe localized attack of second phases of inclusions (stringers) occurred in the following monel alloys: 400, R-405, 500, 501, and 507. The localized corrosion was severe enough to limit the usefulness of these alloys for applications involving long-duration contact with ClF₅. In all cases where comparisons were made, localized corrosion was considerably more severe in moisture-contaminated ClF₅ than in uncontaminated ClF₅.

5) In most cases, corrosion of alloys began with the formation of a passive surface layer, which resulted in weight gain, followed, upon longer exposure, by flaking off of this surface layer, which resulted in weight loss.

6) Raising the test temperatures from ambient to 160°F considerably increased the rate of attack of alloys; the weight change after 30 days at 160°F was more comparable with the weight change after 580 days than 30 days at T_a.

7) There was no noticeable attack on FEP Teflon, TFE Teflon, and Kel-F 81; however, these materials gained considerable weight, compared to the alloys, because of absorption of ClF₅.