JOURNAL OF PROPULSION AND POWER
Vol. 12, No. 1, January–February 1996

Corrosion of Ti-6Al-4V Alloy and 304L Stainless Steel in Liquid Nitrogen Oxides

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Liquid dinitrogen tetroxide is normally stored in stainless steel tanks, whereas the mixed oxides of nitrogen, dinitrogen tetroxide plus nitric oxide, may also be stored in titanium alloy vessels. This article presents new data on the corrosion of unstressed 304L stainless steel and Ti-6Al-4V by these rocket propellant oxidizers at 30°C as a function of time at a surface-to-volume ratio of 6 cm^{-1}. The results show that dry dinitrogen tetroxide (0.003 and 0.02-wt% water equivalent) is the more corrosive medium towards both alloys: the iron oxidation product dissolves more in dinitrogen tetroxide plus 3% nitric oxide, whereas the titanium alloy corrosion products are more soluble in the NO-free medium. However, attack is extremely limited in both oxidizers. It is finished after 550 days (and probably in less than 55 days) in dinitrogen tetroxide and corresponds to the oxidation of a 30- to 40-Å layer of alloy. In dinitrogen tetroxide plus 3% nitric oxide only a fifth of the corrosion takes place, and then within a period of less than 50 days. The results depend substantially on the analysis of the key component metals (Al, Ti, V, Mn, Fe, Cr, and Ni) as determined by state-of-the-art spectrometric methods.

Introduction

THE corrosion of commercially pure titanium and Ti-6Al-4V by liquid oxides of nitrogen was reviewed by us in 1993.[1] There are no reliable data for the rate of corrosion of titanium and its alloys by either NTO (dinitrogen tetroxide, N_2O_4) or MON (mixed oxides of nitrogen, NTO plus nitric oxide). The main preoccupation of the early studies of titanium systems was with stress corrosion cracking (SCC) of the alloy by NTO. The role of elemental oxygen in this process was investigated by Moreland and Boyd,[2] who showed that SCC is inhibited very effectively by NO. Titanium(IV) oxide, TiO_2, is formed on the surface of these metals in contact with air and is also formed in contact with NTO.[1] We would not expect any lower oxidation states of titanium to be stable in the presence of NTO. Apart from TiO_2 no other corrosion products have been identified from the reaction between NTO and elemental titanium; nitric oxide will also be formed. The reactivity of NTO towards TiO_2 is exceptionally low; this must be a kinetic consequence since Ti(IV) nitrates are stable compounds. Evidently the dioxide adheres strongly to the alloy and presents a covering that protects against the corrosive medium; it is therefore important that an earlier description[3] of the appearance at ×500 magnification of the oxide film on Ti-6Al-4V as being flaky must be checked carefully. All previous studies have indicated that the corrosion of Ti-6Al-4V by nitrogen oxides is uniform, a light etching without pitting, although the Ti:Al ratio varies according to the water and chloride content of the oxidizer.[1,3] There is general agreement that the rate of corrosion is very slow and unlikely to lead to structural failure of the unstressed alloy so that the major question relates to flow decay. Our earlier attempts[4] to study the rate of corrosion of Ti-6Al-4V by these oxides of nitrogen yielded ambiguous results: this was in part because the mass losses of the coupons were too small to be sensitive to the extent of corrosion and because the atomic absorption spectrometry (AAS) for Ti, V, and Al were too insensitive.

Two products, not found on the surface, are stable in contact with NTO, namely $TiO(NO_3)_2$ (Ref. 3) and $Ti(NO_3)_4$ (Ref. 4); both are near-white solids, which are readily decomposed by traces of H_2O to TiO_2. The tetranitrate is volatile and ideally should not accumulate in those parts of the rocket motor that are subjected to a vacuum; we would also expect it to react vigorously with hydrazine-based fuels. The oxodinitrate, or its NTO solvate, $TiO(NO_3)_2.N_2O_4$, is less well characterized and probably decomposes to dioxide when heated. Little or nothing is known about either the solubility of any of these titanium compounds in NTO and MON or their reactivity with impurities, such as water. This is unfortunate since oxidizer flow decay could be a problem if significant quantities of insoluble corrosion products were to accumulate in titanium storage tanks and pipelines.

There is no shortage of data on the reactivity of stainless steels with the liquid oxides of nitrogen, although there are several areas where there are serious conflicts as to the rates and ultimate extent of corrosion. Iron(III) and chromium(III) oxides are formed on the surface of these alloys in contact with air and also formed in contact with NTO.[3,5,6] Nickel(II) and manganese(II) oxide are also expected, but have not been detected by x-ray photoelectron spectroscopy (XPS) studies of steel after immersion in nitrogen oxides; Mn is present in 304L steel at about 1.59%, but has never been looked for in our studies as it was thought to be unimportant. The dominant corrosion product derived from ferrous metals was shown by Addison and co-workers to be $Fe(NO_3)_3.1.5N_2O_4$ (Ref. 7). No other product of corrosion has been characterized or even seen in our laboratories. Nearly all of the previous corrosion studies have focused on the mass changes of steel coupons and the quantities of oxidized metal appearing in solution or in suspension. The mass changes are exceptionally small, as we had found earlier, and cannot be reconciled with the quantities of oxidation products. There have been arguments as to the possibility of colloidal materials in the oxidizer solutions and this has led to controversy over the solubility of the oxidized metals. The analytical method used for iron, chromium, and nickel has been AAS in nearly all of the earlier studies. This method,

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Presented as Paper 94-3258 at the AIAA/ASME/SAE/ASEE 30th Joint Propulsion Conference, Indianapolis, IN, June 27–29, 1994; received Nov. 21, 1994; revision received May 30, 1995; accepted for publication July 13, 1995.

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which injects the analyte into a flame and can detect parts-per-million concentrations, has now been superseded by the plasma excitation methods that can detect parts-per-billion levels of many elements, either by inductively coupled plasma mass spectrometry (ICPMS) or by inductively coupled plasma optical emission spectrometry (ICPOES). However, there is general agreement that the extent of corrosion of most steels is trivially small and that the main problem is the accumulation of corrosion products in narrow orifices where they are able to interfere with the flow of oxidizer to rocket engines. It was demonstrated by Blackwell[8] that concentrations of water in excess of 0.24% convert the otherwise crystalline, iron(III) nitrate into a sticky solid or viscous insoluble liquid. Both the crystalline solid and the viscous liquid are believed to be responsible for flow decay in propulsion systems. We have therefore returned to the same problem and have investigated the behavior of the unstressed sheet form of both Ti-6Al-4V and 304L stainless steel in a comparative study involving both NTO and MON-3 using state-of-the-art analytical techniques. The water content of the oxidizers, which can now be determined very reliably,[9] has been varied from 0.003 to 0.15 wt%. This article also provides information on the solubility (particle size less than 40 μm) of the key metals (Al, Ti, V, Mn, Fe, Cr, and Ni) in both NTO and MON-3 at about 15°C and the rate at which the alloy is oxidized; at a later date our study is expected to provide more information on the selectivity of the oxidation of the metals comprising the alloys, but this awaits some surface analyses, which have yet to be completed.

Methods

The intention was to quantify the rate of oxidation of coupons of the two alloys after total immersion in either NTO or MON-3 at 30°C by measuring the total amount of each of the principal elements (Al, Ti, V, Mn, Fe, Cr, and Ni) oxidized as a function of time. As in our previous studies, a known mass of the oxidizer was poured in the liquid phase in vacuo (see Fig. 1) from a glass stock vessel onto a number of chemically cleaned coupons of known mass and geometrical surface area, inside a borosilicate glass corrosion vessel *V*. In this way all air, i.e., additional oxygen, carbon dioxide, or water, was excluded. Two corrosion vessels as well as one blank vessel were loaded in this way for each time interval; the blank vessel contained oxidizer, but no coupons. The vessels were then sealed by fusing the neck of the filling tube and stored at 30°C. At the appropriate time each of the three vessels was opened in vacuo by rupturing the glass break-seal *B* with a glass-encased magnet; the oxidizer was poured through *B* and through a 40-μm sintered glass frit *F* into a receiver *R* and the traces of gaseous nitrogen oxides also transferred from the corrosion vessel to *R* in vacuo (see Fig. 1). The liquid oxidizer in the receiver was allowed to evaporate slowly under reduced pressure at 0°C to leave a residue (scarcely visible to the naked eye) of the dissolved corrosion products. The main chamber *C* of each corrosion vessel was then opened under the protection of a dry nitrogen cover gas and the coupons removed for weighing (±0.05 mg). It was noticed that coupons treated in this way did not release detectable quantities of brown NO_2 on standing. All but one of the coupons in each set were returned to the opened corrosion vessel; these coupons and the inside walls of the vessel were then washed (descaled) with nitric acid (1 wt%), which was also used to dissolve the residue in the receiver. Analysis of the nitric acid for the principal elements was accomplished by ICPMS or ICPOES, as appropriate. Each coupon left unwashed by nitric acid was cut into smaller coupons and stored in a dry container to provide a number of samples for microscopic and surface analysis.

Our earlier studies of this type had used a surface-to-volume ratio (S/V) of 4 cm^{-1}, but the analyses for Al, Ti, Fe, Cr, and Ni by AAS were insufficiently sensitive. The total area of the coupons used in the present corrosion tests was chosen to give a surface-to-volume ratio of 6 cm^{-1} in order to increase the amount of surface oxidation and also the concentrations of metal ions in the final analyte. The increased sensitivity of the ICP spectrometric methods allowed these elements as well as vanadium and manganese to be detected at the 10-ppb level. As a consequence of this we analyzed the contents of 14 corrosion vessels for the dissolved metals content and, separately, for the insolubles. The remaining corrosion vessels were analyzed for their total oxidized metals content. The dissolved metals were taken to be the contents of the filtered oxidizer, i.e., the dry contents of *R* dissolved in the minimum volume of nitric acid (1 wt%); since the material in the receiver had passed through a 40-μm frit we refer to this result as the soluble material. This estimate of the solubility does not refer to 30°C, but rather to a somewhat lower temperature, which we have taken as approximately 15°C, since the solutions had been cooled by the laboratory air as well as by the application of a vacuum. The insolubles were taken to be the nitric acid washings of the coupons and the corrosion vessel walls. The effect of washing a set of chemically cleaned coupons with dilute nitric acid was investigated separately. It was shown that 1-wt% nitric acid behaves as a mild descaling agent for the test coupons after a 5-min contact time.

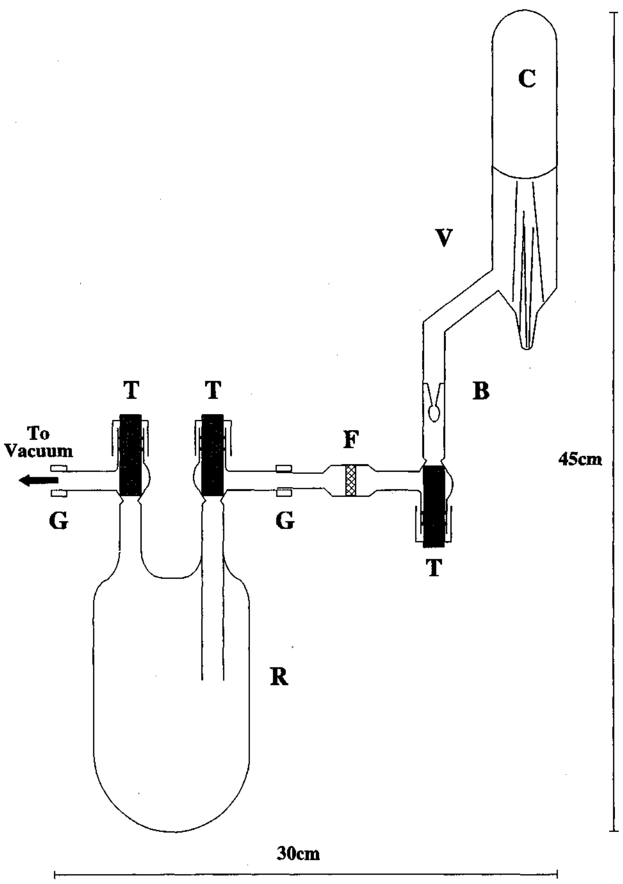

Fig. 1 Filtration of the oxidizer from the corrosion test vessel.

A continuous sampling method was used to follow the corrosion of the titanium alloy in MON-3. The apparatus used consisted of a borosilicate glass vessel, capacity 250 mL, fitted with two greaseless taps: 1) a 40-μm sintered glass frit and 2) two greaseless connectors. The apparatus was kept at 30°C and sampled regularly through the frit; the samples of oxidizer were weighed, allowed to evaporate slowly under reduced pressure, dissolved in 1-wt% nitric acid, and analyzed for the three metals. The residual oxidizer was analyzed similarly and the coupons were descaled with a total of about 90 mL of 1-wt% nitric acid.

Table 1 Oxidizer compositions

Oxidizer	NO, wt%	WE,[a] wt%	Cl^-, wt%	Part,[b] mg/L	Parts per million Fe	Cr	Ni	Mn	Ti	Al	V
MON-3 NAS3620	2.75 ± 0.25	0.17 max	0.04 max	10	0.50	—	—	—	—	—	—
NTO pretest	0	0.003–0.02	0.008	0[c]	0.06	0.00	0.02	0.00	0.00	0.10[d]	0.00
MON-3 pretest	3.0	0.01–0.15	0.008	0[c]	0.05	0.00	0.02	0.00	0.00	0.05[d]	0.00

[a] Water equivalent content.

[b] Particulate content.

[c] Distilled and transferred through a 10-μm frit.

[d] After storage in borosilicate glass at ca. 20°C for ca. 60 days.

Experimental

The corrosion vessels and all other glass apparatus used to contain the oxidizers were treated with nitric acid (50 vol%), blended from 70% analytical grade and nanopure water (minimum specific resistance 18.3 MΩ cm) for 48 h, rinsed with nanopure water to pH 7, dried in an oven at 160°C for 16 h, and then in vacuo. The standard composition of borosilicate glass is given as 2.2 (Al), 1.04 (Fe), 0.1 wt% (Cl), and less than 5 ppm (Cr, Mn).

Dinitrogen tetroxide (>99.5%, Air Products) was dried in the gaseous state by passage through molecular sieve, type 3A, at a rate of ca. 30 g/h. The water equivalent content[9] of the NTO used in this study has been determined by proton (^1H) FTNMR spectrometry to be 0.003 wt%. The chloride content was determined argentimetrically. MON-3 was prepared from carefully dried NTO by the addition of NO (>99.5%, Air Products) until the required increase in vapor pressure had been obtained. The NO content was determined gravimetrically from the oxygen (99.998 vol%, Messer Griesheim) uptake; the water content was found to be 0.01-wt% water. Two other samples of MON-3, containing 0.02 and 0.15-wt% water, were produced by the addition of nanopure water to the 0.01-wt% grade. The initial concentrations of metals in the oxidizers (Table 1) were well within the accepted standards, nevertheless, dummy or blank experiments were set up to provide checks on the concentrations of the metals liberated from the glassware.

The Ti-6Al-4V alloy (typical analyses, Al 6, Fe 0.03, V 4, C 0.02, H 0.01, N 0.01, O 0.065, Ti balance, Goodfellow Metals), in the form of a 0.043-mm-thick foil, temper as rolled, was cut into 0.5 × 5 cm (nominal) coupons: it was then pretreated to remove the impurities introduced during the cutting process as well as to generate a reproducibly uniform surface for the corrosion tests. The multistage pretreatment procedure was comprised of the following[10]:

1) Degrease with isopropanol (Aldrich >99.5% HPLC grade) at ambient temperature (5 min).

2) Clean with 3% aqueous Activax, a proprietary alkaline cleaning agent (Cannings Products), 40°C (15 min).

3) Rinse with nanopure water.

4) Pickle in aqueous nitric (30 vol%, blended from Aldrich 70% AR grade) and hydrofluoric (1.5 vol%, blended from BDH 40% AR grade) acids at 40°C (3 min).

5) Rinse with nanopure water to pH 7.

6) Dry in vacuo.

Sufficient coupons (36) to provide a 170-cm^2 area were used in each corrosion vessel; the mass of oxidizer (ca. 28 cm^3, 40 g) was such that the surface-to-volume ratio was 170/28 ≈ 6 cm^{-1}.

The 304L stainless steel (Cr 18.15, Ni 9.16, Mn 1.59, C 0.02, Si 0.41, P 0.02, S 0.004, Fe balance; Knight Industries, UK) in the form of a 0.18-mm-thick foil, temper as rolled, was cut into 1 × 5 cm (nominal) coupons: it was then pretreated by a multistage procedure comprised of the following[10]:

1) The same 1–3 steps listed earlier.

2) Pickle in aqueous nitric acid (30 vol%, blended from Aldrich 70% AR grade) at 40°C (20 min).

3) Rinse with nanopure water to pH 7 and with isopropanol.

4) Dry in vacuo.

Sufficient coupons (18) to provide 170-cm^2 area were used in each corrosion vessel to achieve a surface-to-volume ratio ≈6 cm^{-1}.

All transfers of the oxidizers, either in the gaseous or the liquid state, were carried out in borosilicate glass apparatus fitted with greaseless fluorocarbon vacuum seals and pistons for vacuum taps (Young's Scientific Glass, London). Where a flexible connection was required this was achieved with 8-mm-o.d. PTFE tubing and two greaseless fittings.

Analyses for metals were carried out in the Laboratories of the National Rivers Authority in Nottingham by ICPMS (Perkin-Elmer Elan 5000) or by ICPOES (Thermo Electron Plasma 300); the detection limits for the seven elements dissolved in 1-wt% nitric acid were approximately 0.06 (Ti), 0.1 (Al), and 0.03 (V), <10 (Fe), 0.02 (Cr), 0.03 (Ni), and 0.04 (Mn) ppb. The concentration of a given metal in the oxidizer of a given corrosion vessel was calculated in two stages. The result obtained, a concentration in 1-wt% nitric acid, was corrected for the background level in the 1-wt% nitric acid itself, and then the difference was converted to a concentration in the mass of oxidizer present in the corrosion vessel containing the coupons. A similar calculation was made for the same element in the corresponding blank vessel to provide the concentration in the mass of oxidizer present in the corrosion vessel containing no coupons. It is then meaningful to subtract these two concentrations to obtain a corrected concentration of the element in the oxidizer. Some corrected values appeared as negative quantities; in all but one instance the results concerned aluminium and must be attributed to the slow attack of the oxidizer on the borosilicate glass, Al content 2.2 wt%. Our data indicate that movement of the key elements was occurring into as well as out of the glass. This is not really surprising; no self-respecting analyst would expect solutions at these low concentrations to remain unchanged in glass vessels for these periods of time.

Coupons were weighed in a ground-glass-capped weighing bottle on a Sartorius 2004 MP five-decimal-place balance, capable of weighing to ±0.05 mg. In the earliest stage of this program the changes in coupon masses were monitored on a regular basis; it was soon evident that the changes were comparable with the experimental error associated with the analytical balance. From the worst case data presented in Table 2 for NTO, 0.003-wt% water, where the total amount of the three metals lost (8.82 + 1.46 + 0.91 + 0.15 = 11.34 ppm) multiplied by the mass of oxidizer (46 g) amounts to 0.52 mg, it is evident that the expected mass changes are not likely to be experimentally significant under our conditions.

Results

Corrosion by NTO at 30°C, *S/V* 6-cm^{-1} Water Content 0.003 wt%

Ti-6Al-4V

The total quantities of corrosion products, as determined by analyses for titanium and vanadium, after 552 and at 821 days immersion were found to be the same within experimental error, i.e., there was no further corrosion occurring in the system

Table 2 Extent of corrosion of 304L stainless steel in NTO and in MON-3 at 30°C in borosilicate glass vessels

Oxidizer	WE,[a] wt%	Test duration, days	Total quantity of element oxidized, ppm[b] Fe	Cr	Ni	Mn
NTO	0.003	553–822	8.82 ± 0.14	1.46 ± 0.15	0.91 ± 0.07	0.15 ± 0.01[c]
NTO	0.020	55–88	7.95 ± 0.36	1.77 ± 0.07	1.02 ± 0.07	0.17 ± 0.01
MON-3	0.010	49–397	1.31 ± 0.16	0.02 ± 0.01	0.11 ± 0.02	0.03 ± 0.01
MON-3	0.020	41–332	1.59 ± 0.13	0.03 ± 0.01	0.13 ± 0.02	0.04 ± 0.00

[a] Water equivalent content.
[b] Expressed as a concentration in ca. 40-g oxidizer from 170-cm^2 coupon area.
[c] After 822 days immersion; no determinations after 553 days.

Table 3 Extent of corrosion of Ti-6Al-4V alloy in NTO and in MON-3 at 30°C in borosilicate glass vessels

Oxidizer	WE,[a] wt%	Test duration, days	Total quantity of element oxidized, ppm[b] Ti	Al	V
NTO	0.003	552–821	3.46 ± 0.50	0.42 ± 0.01	0.58 ± 0.02
NTO	0.020	55–88	6.91 ± 0.30	0.31 ± 0.01	0.84 ± 0.14
MON-3	0.010	49–397	0.17 ± 0.03	[c]	0.01 ± 0.00
MON-3	0.020	41–335	0.14 ± 0.01	[c]	0.01 ± 0.00
MON-3	0.150	43–368	0.21 ± 0.01	[c]	0.01 ± 0.00

[a] Water equivalent content.
[b] Expressed as a concentration in ca. 40-g oxidizer from 170-cm^2 coupon area.
[c] Attack on glass caused variable and high blank analyses.

Table 4 Solubilities of titanium, aluminium, vanadium, iron, chromium, nickel, and manganese in NTO and in MON-3 at ca. 15°C

Oxidizer	WE,[a] wt%	Apparent solubilities[b] in oxidizer, ppm Ti	Al	V	Fe	Cr	Ni	Mn
NTO	0.003	3.86	[c]	0.54	0.26	0.03	0.00	0.00
NTO	0.020	6.60	0.00	0.80	0.30	0.00	0.00	0.00
MON-3	0.010	0.01	0.00	0.01	1.27	0.00	0.00	0.00
MON-3	0.020	0.00[d]	0.05[d]	0.01[d]	[e]	[e]	[e]	[e]
MON-3	0.150	0.00	[c]	0.01	[e]	[e]	[e]	[e]

[a] Water equivalent content.
[b] Oxidizer from corrosion vessel initially at 30°C filtered through a 40-μm sintered glass frit into an evacuated receiver vessel.
[c] Attack on glass caused variable and high blank analyses.
[d] Derived from short-term study.
[e] Not studied.

after 552 days (Table 3). Furthermore, no corrosion products were visible, either on the glass surfaces or on the surface of the metal coupons, even after cooling the oxidizers to 0°C. This contrasts with the behavior of stainless steel in NTO where crystals were visible to the naked eye. The solubilities of titanium and vanadium in NTO, after filtration at approximately 15°C, were estimated to be 3.86 and 0.54 ppm, respectively (Table 4). The total extent of corrosion was only marginally greater, i.e., it would have resulted in the following concentrations in solution: Ti, 3.46 ± 0.50; V, 0.58 ± 0.02 ppm. Problems were encountered with the results for aluminium in these longer term studies; the analyses of oxidizer in the coupon-free (blank) vessels gave variable and often unacceptably high values for this element, probably as a result of ion exchange with the Pyrex® glass, which contains aluminium.

304L SS

The total quantities of the corrosion products after 553 and 822 days immersion were found to be the same within experimental error, i.e., there was no further corrosion occurring in the system after 553 days (Table 2). At least two kinds of crystalline corrosion products were visible, both on the glass surfaces and on the surface of the metal coupons, especially after cooling the oxidizers to 0°C. These were amber-colored crystals, similar to the solvated iron(III) nitrate,[7] and green crystals. This contrasts with the behavior of Ti-6Al-4V in NTO where no crystals were visible to the naked eye. The solubilities of iron, chromium, nickel, and manganese in NTO, after filtration at approximately 15°C, were estimated to be 0.26, 0.03, 0.00, and 0.00 ppm, respectively (Table 4). The total extent of corrosion was substantially greater, i.e., it would have resulted in the following concentrations in solution: Fe, 8.82, Cr, 1.46, Ni, 0.91, and Mn, 0.15 ppm (Table 2). No results for manganese were requested from the analysts for the 553-day studies, since we were not aware that this element would prove to be significant.

Corrosion by NTO at 30°C, S/V 6 cm^{-1} Water Content 0.02 wt%

Ti-6Al-4V

This study was deemed necessary in order to find out how much corrosion had occurred on a shorter time scale. Five corrosion vessels were loaded with NTO containing marginally more water (0.02 wt%): three vessels, one blank and two with coupons, were opened after 55 days and the other two, one blank and one with coupons, after 88 days. Corrosion of the coupons (Table 3) was the same within experimental error for all three vessels. The total amount of corrosion was greater for all three elements than with the more dry grade of NTO and, since the aluminium levels in the blank vessels were plausibly lower, the results for aluminium are also quoted in Table 3. The solubilities of the three elements (Table 4) are also higher for NTO with this higher water content.

304L SS

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Corrosion by MON-3 at 30°C, *S/V* 6 cm^{-1} Water Contents 0.01, 0.02, and 0.15 wt%

Ti-6Al-4V

The longer term study of these systems has provided corrosion data for coupons in these three grades of MON-3 immersed for between 41–397 days; the results are based upon 30 corrosion vessels, including 9 blank vessels, and imply that corrosion had totally ceased before the first corrosion vessel was opened after 41 days. There was no significant effect of the water contents in the three grades of MON-3 used. The extent of corrosion was substantially less than that in NTO (Table 3) and the total amounts of the metals determined were as follows: Ti, 0.21; V, 0.02 ppm. Since there were no visible signs of corrosion products on the coupons, it was assumed at first that these values represented estimates of the solubilities of these elements in MON-3, however, analyses of the filtered MON (Table 4) showed that titanium, vanadium, and, probably, aluminium are essentially insoluble in MON-3.

Corrosion by MON-3 at 30°C, *S/V* 6 cm^{-1} Water Contents 0.01 and 0.02 wt%

304L SS

The long-term study of these systems has provided corrosion data for coupons immersed for between 41–397 days in the two drier grades of MON-3; the results are based upon 19 corrosion vessels, including 6 blank vessels, and imply that corrosion had totally ceased before the first corrosion vessel was opened after 41 days. There was no significant effect of the water contents in the two grades of MON-3 used. The extent of corrosion was one-fifth of that in NTO (Table 2). There were no visible signs of crystalline corrosion products on the coupons.

Corrosion by MON-3 at 30°C, *S/V* 3.74–6.59 cm^{-1} Water Content 0.02 wt%

Ti-6Al-4V

The results of the short-term study, up to 73 days, using MON-3 containing 0.02-wt% water, show that the concentration of titanium in the portions of oxidizer, filtered through a 40-μm frit, remained steady at a value of around 0.002 ppm; this is identical to that found in the longer-term studies after 45 days, and so reflects the actual solubility of the titanium corrosion product in MON-3 at ca. 30°C. The concentrations of aluminium (0.045 ppm) and vanadium (0.007 ppm) derived from this short-term study also appear to represent meaningful solubility data (Table 4). These saturation levels were reached within one day of setting up the experiment at a surface-to-volume ratio of 3.74 cm^{-1}. The cumulative quantities of the metals, corrected for any additional attack by the 1-wt% nitric acid correspond to 0.18 (Ti), 0.00 (Al), and 0.00 ppm (V) referenced to the original amount of oxidizer: these quantities are in excellent agreement with the results given in Table 3 for MON-3.

Discussion

This study of the corrosion of the alloys by the liquid nitrogen oxides was planned to provide information about the total amount of each of the principal elements oxidized. The solution of the corrosion product in the oxidizer was filtered and the involatile residue, dissolved in 1-wt% nitric acid, analyzed. It was also decided to capture any corrosion products deposited on the walls of the apparatus, including the frit, as well as any on the coupons. For this reason both the coupons and the walls of the corrosion vessels were washed with dilute nitric acid (1 wt%). The process of washing the coupons may be described as a descaling process. Correction has been made for this in the data shown in Tables 2 and 3. We also note that the effect of using 1-wt% nitric acid to descale pretreated coupons is to dissolve iron and, to a lesser extent, nickel, preferentially from the steel and to remove aluminium and, to a lesser extent, vanadium, preferentially from the titanium alloy. This is noteworthy because the pretreatment process itself will have caused a significant alteration in the composition of the surface of the coupons.

It has been pointed out that one coupon of each set of coupons was left unwashed for later surface characterization. It was not considered necessary to correct the analytical results for this since maximum error involved here is less than 5.6%.

Ti-6Al-4V

The results show that the corrosion of this alloy by both oxidizers proceeds to a limited extent and then stops. This halt is not a balance between the rate of further attack on the alloy and the rate of ion exchange with the glass apparatus, because we have observed higher concentrations of dissolved species in NTO, the more corrosive medium, than in MON. At 30°C and at a surface-to-volume ratio of 6 cm^{-1}, the oxidation appears to be complete within a period of less than 55 days (for NTO) and of less than 41 days (for MON-3). We find that the solubility of the main corrosion product, derived from titanium, in NTO is relatively high. The results in Tables 3 and 5 clearly indicate that vanadium is being preferentially oxidized as compared with titanium; the behavior of aluminium, less obvious because of the problems with high background levels, is more similar to that of titanium, allowing for the relative amounts in the alloy. It appears that the effect of the water in the two batches of NTO used in this study is rather considerable and merits further examination. Our view is that there is another parameter that has yet to be identified. Apart from the known problem with stress corrosion cracking, our results show that there is no reason why dry NTO, stored in vessels made of Ti-6Al-4V, should lead to flow decay problems. Viewed in terms of uniform corrosion, the extent of reaction corresponds to about 30 Å (3 nm), which is the thickness of the air-formed oxide layer on this alloy.

The extent of corrosion in MON-3 appears to be unaffected by the water equivalent content in the range 0.01–0.15 wt%, nor is it limited by the solubility of the corrosion product. The data in Tables 3 and 5 show that the rate of attack on the alloy

Table 5 **Time-averaged corrosion rates of Ti-6Al-4V alloy in NTO and in MON-3 at 30°C**

Oxidizer	WE,[a] wt%	Time, days	Corrosion rate,[b] mpy $\times 10^6$		
			Ti	Al	V
NTO	0.003	552	45[c]	95[c]	205[c]
NTO	0.020	55	1060	813	3230
MON-3	0.010	49	42	51	73
MON-3	0.020	41	36	98	67
MON-3	0.150	43	47	[d]	90

[a] Water equivalent content.

[b] Time-averaged value allowing for the fractional composition of the element.

[c] Corrosion probably complete before vessel opened after 552 days.

[d] Attack on glass caused variable and high blank analyses.

is similar for each of the three main metals, although there is a slight preference for vanadium as compared with the other two. If the time-averaged corrosion rates (thousandth of an inch per year) in Table 5 are converted to extents of penetration when corrosion stops, after ca. 50 days, then it appears that, on average, less than one atomic layer has been oxidized. Although the titanium corrosion product is less soluble in MON than in NTO, the quantity of oxidation product is so small that it is unlikely to cause flow decay.

304L SS

The results show that the corrosion of 304L stainless steel by both oxidizers proceeds to a limited extent and then stops. We believe that this halt is not a balance between the rate of further attack on the alloy and the rate of ion exchange with the glass apparatus, by analogy with the parallel study of the corrosion of Ti-6Al-4V. At 30°C and at a surface-to-volume ratio of 6 cm^{-1}, the oxidation appears to be complete within a period of less than 55 days (for NTO) and of less than 41 days (for MON-3). Analogous behavior has been observed by Ally and Heubusch[1] as well as by us for Ti-6Al-4V alloy in these media. More recently, Mellor and co-workers[11,12] have published results for MON-1 and MON-3 corrosion of steels, which are compatible with an early cessation of the corrosion processes, except at the highest levels of water concentration.

We find that the solubility of iron, the main product of corrosion of stainless steel, in NTO is relatively low, although the other metals are even less soluble. The results in Tables 2 and 6 clearly indicate that all four transition metals are being oxidized in NTO at comparable rates, allowing for the composition of the alloy. Our results show why dry NTO, stored in vessels made of 304L, might suffer flow decay problems, even though the extent of corrosion corresponds only to about 25–40 Å, i.e., comparable to the thickness of the air-formed oxide layer on this alloy. The identity of the colored crystals has yet to be investigated; the amber-colored product appeared to be the dominant one and from its color alone it must be the iron flow decay compound, $Fe(NO_3)_3.1.5N_2O_4$. The color of the other product is similar to that expected for either a nickel(II) or a chromium(III) nitrate and, moreover, we know that both chromium and nickel are being oxidized in comparable amounts; the matter clearly requires further study.

The ultimate extent of corrosion in MON-3 appears to be little affected by the water equivalent content in the narrow range 0.01–0.02 wt%, nor is it limited by the apparent solubility of the corrosion products. The data in Tables 2 and 6 show that the rate of attack on the alloy is similar for iron, nickel, and manganese, although iron is the most abundant. If the time-averaged corrosion rates (mpy) in Table 6 are converted to extents of penetration when corrosion stops, after ca. 50 days, then it appears that about three atomic layers have been oxidized on average. The iron corrosion product is five times more soluble in MON than in NTO at ca. 15°C so that nearly all of the iron that has been oxidized appears in solution. Thus, the total quantity of iron found (i.e., in solution and on the coupon/glass surfaces), 1.70 ± 0.16 ppm, minus the nitric acid descaling correction (0.394 ppm) is similar to the apparent solubility, 1.27 ppm. Mellor and co-workers[12] have reported a similar amount of oxidized iron produced by 304L steel in MON-3 at 30°C, surface-to-volume ratio 8.8 cm^{-1}; their results did not change significantly over between 20–100 days, thus supporting our view that corrosion has halted on or before 41 days. They did not detect a significant difference for two low (0.008 and 0.018 wt%) levels of water content; however, higher water contents boosted the corrosion observed. It is noteworthy that our chemical studies confirm that chromium is oxidized to a smaller extent than the other three metals; this is in line with the surface studies that indicate[12] enrichment of chromium on surfaces that have been immersed in MON. Mellor has also investigated the solubility of iron in MON-3, containing 0.01-wt% water, in terms of the particle sizes and has reported a value of 0.8 ppm for total solubility (>10 μm) at both 25 and 35°C (Ref. 13).

Table 6 Time-averaged corrosion rates of 304L stainless steel in NTO and in MON-3 at 30°C

Oxidizer	WE,[a] wt%	Time, days	Corrosion rate,[b] mpy × 10^6			
			Fe	Cr	Ni	Mn
NTO	0.003	553	102[c]	66[c]	83[c]	70[c,d]
NTO	0.020	55	900	749	850	803
MON-3	0.010	49	210	14	126	175
MON-3	0.020	41	292	21	177	229

[a] Water equivalent content.
[b] Time-averaged value allowing for the fractional composition of the element.
[c] Corrosion probably complete before vessel opened after 553 days.
[d] Estimated from datum at 822 days.

Our rationalization of the different solubilities of the corrosion products is that titanium(IV) and vanadium(V) nitrates are soluble in NTO because they are low lattice energy compounds of high volatility; indeed we have evidence that these two compounds are more highly soluble in pure NTO than the data in Table 4 show.[5,14] On the other hand the metal(II) and metal(III) nitrates, such as are produced by the oxidation of stainless steel, are more ionic and, having higher lattice energies, are less likely to dissolve in the nonionic solvent NTO. The effect on solubilities of adding a relatively low concentration of nitric oxide to NTO is at least twofold: on the one hand NO reacts with several nitrates as in Eq. (1) to produce oxonitrates in a solvolysis reaction and also NO enhances the dielectric constant of the medium, and thus, enhances its ability to dissolve ionic compounds. It may well be that this should be viewed as the interaction of NO with the NO^+ ion of a NTO solvate, $NO^+\ Fe(NO_3)_4^-$, Eq. (2):

$$2Ti(NO_3)_4 + 2NO \rightarrow 2TiO(NO_3)_2 + 3N_2O_4 \qquad (1)$$

$$NO + NO^+Fe(NO_3)_4^- \rightarrow N_2O_2^+Fe(NO_3)_4^- \qquad (2)$$

Acknowledgments

This work has been supported by the Procurement Executive, Ministry of Defence, United Kingdom. The authors extend their thanks to the Defence Research Agency at Farnborough, Hampshire, for permission to publish this article, to Malcolm Fiddick, D.R.A., for encouragement, and to P. J. Boden and many other colleagues at the University of Nottingham. This paper is dedicated to the memory of Cliff Addison.

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1995, 650 pp, illus, Hardback
ISBN 1-56347-118-3
AIAA Members $89.95
List Price $104.95
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