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April 11, 1966
DMIC Technical Note

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AUG 16 1968

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STRESS CORROSION OF Ti-6Al-4V IN LIQUID NITROGEN TETROXIDE

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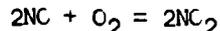
This note was prepared to document the recent finding that the Ti-6Al-4V alloy is susceptible to stress-corrosion cracking in some grades of nitrogen tetroxide, N_2O_4 , and to describe briefly the work that is now going on to define the critical parameters involved in this phenomenon. Previously titanium and its alloys were believed to be compatible with N_2O_4 . In the absence of stress, titanium shows almost no corrosion in liquid or gaseous N_2O_4 in tests to 165 F. (1)*** Although titanium is impact sensitive at high impact levels, (2) no propagation of the reaction is reported.

The first reported indication of stress-corrosion failure came in early 1965 when a pressurized Ti-6Al-4V (solution-treated and aged) tank filled with liquid N_2O_4 ruptured at Bell Aerosystems Company. (3) Failure came after 40 hours' exposure at 105 F and a stress level of 90,000 psi. Microscopic examination of the tank disclosed a considerable number of cracks which had formed in all areas where the stress level was above 40,000 psi.

Following this discovery, NASA instituted a program to investigate the failure. A literature survey and a test program using tanks and test coupons was undertaken. Over 20 aerospace companies, government agencies, research firms, and universities are cooperating in this study which is being coordinated by The Bell Aerosystems Company for the National Aeronautics and Space Administration.

Some of the test results available to mid-March of 1966, are summarized in Tables 1 and 2. On the basis of these and other studies, the following conclusions can be made:

- (1) Stress-corrosion cracking will usually occur in N_2O_4 when no significant or measurable amounts of NO are present and the system is exposed to moderately high stresses at temperatures in the range of 85 F to 165 F.
- (2) Stress-corrosion cracking does not occur in N_2O_4 when the N_2O_4 contains an excess of NO.
- (3) NO and O_2 are mutually incompatible, i.e., both cannot exist at the same time in N_2O_4 . The following reaction is believed to occur:



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*** References cited are presented at the end of this note.

TABLE 1. TESTS IN TANKS PRESSURIZED TO 250 PSIG, EQUIVALENT WALL STRESS OF 90,000 PSI

Tanks	Propellant	Temperature, F	Time to Failure
(1) Ti-6Al-4V	Red ^(a) N ₂ O ₄	85	200 hours
(2) Ti-6Al-4V	Ditto	90 ± 8	51 to 192 hours
(3) Ti-6Al-4V	"	105	14 to 127 hours
(4) Ti-6Al-4V	"	160	6 to 12 hours
(5) Ti-6Al-4V + TEFLON bladder	"	105	23 days
(6) Ti-6Al-4V (shot peened)	"	105	None after 30 days
(7) Ti-6Al-4V	Green ^(b) N ₂ O ₄ + 1% NC	160	Ditto
(8) Ti-6Al-4V	Green ^(b) N ₂ O ₄ + 0.3% NC + 0.08% Cl	-	"

- (a) "Red" N₂O₄ is conventionally prepared by bubbling oxygen through "green" N₂O₄. See Table 3 for specifications.
- (b) "Green" N₂O₄ contains some NC. The composition of currently approved MSC-PPD-2 grade is given in Table 3.

TABLE 2. TESTS OF SPECIMENS

Specimen(a)	Propellant	Temperature, F	Time to Failure
(1) Stressed	Red N ₂ O ₄	165	90 hours or less
(2) Stressed	N ₂ O ₄ + NC (0.1 to 1.7%)	Ditto	No failure in 120 hours
(3) Stressed	N ₂ O ₄ + H ₂ O (0.2 to 1.1%)	"	Ditto
(4) Stressed	N ₂ O ₄ + FNA (25% H ₂ O)	"	"

- (a) Stress varied from 90 ksi to 140 ksi.

TABLE 3. COMPOSITION OF N_2O_4 (a)

Element	Content, wt/%	
	Requirements of MIL-P-26539 A	Requirements of NASA MSC-PPD-2
N_2O_4	99.5 minimum	99.5 minimum
H_2O (as HNO_3)	0.1 maximum	0.1 maximum
Cl (as $NCCl$)	0.08 maximum	0.08 maximum
NC	-	0.6 ± 0.20
Particulate matter	10 mg/c maximum	10 mg/c maximum

- (a) In this work, the MIL-P-26539A grade has been called "red" and/or "white" while the MSC-PPD-2 grade "green". These designations arise from the color differences in various grades of N_2O_4 at 0 C. Thus, at 0 C, N_2O_4 of the MSC-PPD-2 grade is bluish-yellow or green while N_2O_4 containing no measurable NC content is yellowish or straw colored, i.e., 'red' or 'white' in comparison to the MSC-PPD-2 grade. At room temperature, all grades of N_2O_4 (including the MIL-P-26539A and MSC-PPD-2) are reddish-brown in color.
- (4) The commercial and military specifications to which N_2O_4 is processed do not control either its O_2 or NC content. As a result of this work, NASA has developed a specification for N_2O_4 which controls the NC content. See Table 3.
 - (5) Stress-corrosion cracking in "red" N_2O_4 shows a time temperature dependence as indicated in Table 1.
 - (6) A TEFLON bladder is used in some of these tanks to contain the N_2O_4 . The TEFLON acts as a barrier but is permeable, in time, to N_2O_4 . On occasion, tanks containing TEFLON bladders filled with red N_2O_4 have failed after extended periods of time (see Test 5 in Table 1) and these have shown the same type of failure as where no bladder was used.
 - (7) Shot peening the inside surface of a tank so that there is no tensile stress on the inside diameter surface of the tank shell when in N_2O_4 service reduces the probability of stress-corrosion cracking.
 - (8) All tests to date have shown complete inhibition of stress-corrosion cracking of titanium in "green" N_2O_4 (See Table 3).
 - (9) Chloride addition as $NCCl$ to "green" N_2O_4 up to the specification limit of 0.08 percent apparently does not initiate stress-corrosion cracking. (See Test 8, Table 1.)

- (10) Further work has indicated that additions of sufficient water to red N_2O_4 will eliminate the stress-corrosion cracking of titanium. (This, in effect, adds NO and eliminates free oxygen since water forms nitric acid and NO in N_2O_4 .)

Other work has shown that the primary cause of cracking is not related in any way to any titanium processing operation. All normally accepted cleaning, heat treating, aging, welding, descaling, and handling techniques used for titanium have been checked. The stress-corrosion cracking susceptibility was not affected by any variation in these processes.

The crack propagation behavior of titanium in red N_2O_4 as compared with that for other environments was investigated in studies at Battelle for DMTC.⁽⁴⁾ These tests were performed using a pre-fatigue-cracked specimen loaded dynamically under 3-point loading in an autoclave with a technique similar to that used in seawater tests as discussed by Brown.⁽⁵⁾ Briefly, the specimens are step-loaded to a higher stress level every 4 to 8 minutes until failure occurs. The stress level is measured by the stress intensity factor, K, in ksi $\sqrt{\text{inch}}$, assuming conditions of plane strain.

In air, step-loading resulted in failure at 70 ksi $\sqrt{\text{inch}}$. Similar results were found using the same techniques with red N_2O_4 . However, when a specimen was step-loaded to just below the air value, and held for several days in red N_2O_4 , stress cracks formed throughout the specimen and failure of the specimen occurred after 12 days at 127 F. During the experiment, relaxation of the stress was noted, indicating slow propagation of a crack, and the stress level had to be adjusted throughout the exposure period.

These results show that the rate of propagation of stress cracks is quite slow in N_2O_4 as compared with seawater. Time of exposure to the environment is, therefore, a much greater factor than it is in salt water, for example, where stress-corrosion failure can occur in a few minutes for some titanium alloys. Thus, the experimental procedure must be modified to evaluate stress-corrosion cracking in red N_2O_4 by the precracked specimen method.

In other short-term studies using precracked specimens, additions of 0.5 percent water (forming nitric acid and NO) and 0.25 percent concentrated hydrochloric acid (adding chlorides and water) were made to N_2O_4 . The results again were similar to those in air.

Although the mechanism of stress-corrosion cracking of titanium in N_2O_4 is not fully understood, it is apparent that oxygen activity plays an important role, and that additions of NO inhibit the attack. It has been suggested that stress-corrosion cracking occurs on the titanium surface at coarse slip lines where the oxide film is not protective, or is easily ruptured, such as by local creep. This would account for the network of cracks associated with the failures. The NO addition could prevent this attack by removing the active oxygen and/or absorbing on the surface as a protective film. Chlorides have been suggested as a possible cause, since they are often associated with cracking. However, no proof of their contribution to the mechanism of cracking has been found. Work is continuing in these areas.

Further work is also indicated in the determination of what other alloys of titanium are susceptible, and on the character of the metal surface before and after exposure to N_2O_4 .

ACKNOWLEDGMENTS

The authors are indebted to Messrs. R. E. Johnson, Head of the Manufacturing and Materials Group, NASA MSC, G. F. Kappelt, Chief Engineer of the Laboratories and Test Department of Bell Aerosystems Company, and L. J. Korb and R. E. O'Brien, Supervisor and Research Specialist, respectively, of the Apollo Metals Structural Sciences group in the Space and Information Division of North American Aviation for their cooperation in providing much of the data which are summarized herein. They are also grateful to the National Aeronautics and Space Administration and to North American Aviation for their permission to release this information to DMIC.

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