NASA

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

A Case History of Titanium Stress Corrosion in Nitrogen Tetroxide

Robert E. Johnson, George F. Kappelt, and Larry J. Korb

MANNED SPACECRAFT CENTER
HOUSTON, TEXAS

20

A Case History of Titanium Stress Corrosion in Nitrogen Tetroxide

Robert E. Johnson, George F. Kappelt, and Larry J. Korb

An investigation of the incompatibility of titanium in certain grades of nitrogen tetroxide will be discussed as a case history. The methodology used in its resolution will point out some of the dangers associated with compatibility testing. The methodology also will present some of the difficulties associated with coordinating an investigation involving many contractors and U. S. Government agencies. The techniques employed in this investigation are described in considerable detail for the benefit of investigators with similar problems.

Robert E. Johnson is Head, Materials Technology, National Aeronautics and Space Administration, Manned Spacecraft Center, Houston, Texas; George F. Kappelt is Chief Engineer, Laboratories and Test Department, Bell Aerosystems Company, Buffalo, New York; and Larry J. Korb is Supervisor, Metallics Group, North American Aviation, Inc., Downey, California. This paper is scheduled for the 1966 National Metals Congress, Chicago, Illinois.

One of the most desirable rocket propellant systems in use at the present time is the hypergolic system involving a fuel and a strong oxidizer, such as aerozene 50 and nitrogen tetroxide (N_2O_4). In the Project Apollo of the National Aeronautics and Space Administration (NASA), the aerozene 50/N_2O_4 system is used for the main propulsion systems, as well as the attitude control (reaction control) systems. The Project Apollo lunar module descent and ascent stages and the reaction control system (RCS) depend upon this propellant system. The Saturn booster and the Lunar Orbiter vehicle use this system for attitude control. The NASA Gemini and Surveyor Programs and the Air Force transtage of the Titan III booster system also use this propellant system. All of these systems require a highly efficient pressure vessel for propellant storage since a number of the tanks are quite large, and it is essential to minimize weight.

Early Compatibility Testing

The use of the hypergolic propellant in many NASA and Air Force programs required a considerable amount of testing under varied conditions to determine the compatibility of the metallic and the nonmetallic materials to be used in these systems. As a result of these tests, the titanium alloy, Ti-6Al-4V, was chosen to contain the fuel and the oxidizer. The material was solution treated and aged to give an ultimate tensile strength of 160,000 psi, and a yield strength of 150,000 psi with approximately 8% minimum elongation (in 2-inch gage lengths).

Several investigators (1,2) had shown the reactivity of titanium alloys in strong oxidizers such as red fuming nitric acid, liquid fluorine, and liquid oxygen. The corrosion and impact sensitivity of titanium alloys in N_2O_4 were investigated under Air Force studies as early as 1960 (3,4). To evaluate the use of these alloys for the Project Apollo, the prime contractor, North American Aviation, Inc., Downey, California (NAA), undertook an extensive series of tests on Ti-6Al-4V in N_2O_4 ranging from the effects of water content, time of exposure, mill product form, welding, stress (up to 90% tensile yield strength), galvanic couples, elevated temperatures (up to +140° F), surface finish, and impact loading under varying conditions. The results of these tests, published in September 1963 (5), indicated no serious compatibility problem and only a slight impact sensitivity under high energy levels, as was reported by the earlier investigators. Therefore, the titanium alloy, Ti-6Al-4V, was declared compatible with N_2O_4 and approved by NASA for these applications. Significantly, all N_2O_4 used in this investigation was procured and analyzed in accordance with the Military Specification MIL-P-26539A "Propellant, Nitrogen Tetroxide." The analysis of this propellant, as required by this specification, is shown in Table 1.

Description of Early Test Failures

In early 1964, two Apollo main propulsion system titanium alloy tanks successfully completed 30-day exposures to N_2O_4 under maximum operating stress (approximately 100 ksi wall stress). These tanks were about 51 in. in diameter, about 14 ft in length, approximately 0.055 in. in wall thickness. However, in January 1965, a smaller, RCS titanium alloy tank failed a similar 30-day test at approximately the same stress level. Failure analysis by the subcontractor, Bell Aerosystems Company (Bell), and the prime contractor, NAA, concluded that the failure mode was stress corrosion and the probable cause was contamination (possibly chlorides) prior to heat treatment. Six cracks were observed in three discrete areas of the tank wall. This tank had an inner Teflon bladder which, theoretically, isolated the titanium from the N_2O_4. To be safe, however, 10 additional tanks (without bladders) were put into test at Bell to represent a sampling of production runs to ensure that the contamination problem was an isolated one, or associated with a particular production period. Thirty-four hours after the tanks had reached test temperature (105° F) and pressure, the first tank failure occurred. Three other tanks burst in the next 9 hours of test. Photographs of the test failures may be seen in Figs. 1 and 2. When the failed tanks were examined metallurgically, thousands of stress corrosion cracks per tank were found. These cracks varied from very shallow (0.003 in.) to cracks extending through the 0.017-in. thick wall. Photomicrographs of these cracks may be seen in Figs. 3 and 4. Other tank tests subsequently showed a strong time-to-failure dependence with the temperature, and a definite relationship with the stress level. The NASA and the Apollo contractors were faced with a serious material problem in a proven application.

Initial Studies

At this point, the investigators decided not to alert the industry because of the confidence in the earlier compatibility tests, and the success of the main propulsion tank tests in 1964. Several hypotheses of failure were postulated. These included: 1) contamination in the test equipment, 2) galvanic corrosion (due to the presence of stainless steel and aluminum in the systems internal to the tanks), and 3) contamination in the manufacturing process.

Test Approaches

Two approaches were undertaken to determine the cause of these tank failures since the investigators still did not believe a general incompatibility existed between titanium alloys and N_2O_4. One approach was to simulate the failure in the laboratory, and the second, to investigate detailed testing and processing procedures. (For later reference, the test centers involved at this point were NAA, Bell, and the NASA, Manned Spacecraft Center.) In the first approach, Bell personnel initiated a coupon test program using standard stress corrosion U-bend samples in N_2O_4 with no initial failures, even at stresses considerably higher than those in the wall at tank failure. However, modification of the testing technique soon resulted in reproducible failures. At the same time, NAA put two Apollo tanks and numerous coupons into test under identical stress, temperature, and military-specification N_2O_4 test conditions.

In the other approach, teams from Bell and NAA surveyed every step in the processing of these tanks and compared these with steps used in the fabrication of the main propulsion tank and other successful tank applications, such as those of the NASA Gemini and Surveyor Programs and the Air Force transtage of the Titan III booster.

These investigations, although carefully planned, only confused the issue. For example, the tanks and coupons under test in California did not fail, and only minor differences in processing were noted by the fabrication survey. The chloride content of the air in the vicinity of the Bell test cells, due to the concentration of chemical industries in the area, was given consideration. Additional help was enlisted in the effort. The material supplier, Titanium Metals Corporation of America (TMCA), was asked to provide support; and additional consulting support, from Ohio State University and Union Carbide and Carbon Company, Buffalo, New York, was obtained.

The investigators noted that the small Apollo tanks differed from all other tanks in that the natural oxides formed during aging or stress relieving were removed from the tanks which failed and left intact in the tanks made for other applications. To determine the magnitude of this problem to the space programs, NASA directed that tanks made for the Gemini and Surveyor Programs also be put into test at Bell. The tanks were tested under the Apollo test conditions which exceeded the requirements in the Gemini and Surveyor Programs, and the tanks failed in a pattern consistent with the other Apollo tanks. Thus, the fact that they failed had no implication on the worthiness for which they were designed, but the failures were significant in that they showed the RCS tanks were not unique.

Another tank was put into test to evaluate the effect of eliminating the galvanic couple. It also failed in a similar manner. At this point, it was obvious that the test procedure was not at fault, that manufacturing steps did not contribute significantly, and that galvanic corrosion did not occur. This meant a general incompatibility existed between the tank material and the test fluid. The technical Apollo stress-corrosion problem now became a significant aerospace problem, with the coordination and administration problems faced by NASA rapidly overshadowing the technical evaluations.

Problems of Program Administration

Many inquiries were received by NASA concerning the incompatibility of the titanium hardware designed for N_2O_4 with aerozene 50 and other fluids. In an effort to inform the community, NASA was host at a meeting at the Manned Spacecraft Center, Houston, Texas, to describe the problem as it was known at that time. Some 57 engineers and scientists representing 26 interested organizations responded. Some of the organizations began limited test programs after the details of the problem were released. NASA personnel were directed to use every available resource to solve the problem since the dollars involved (Project Apollo hardware in inventory was valued at approximately $45 million) and the potential slip in schedule could jeopardize the entire Project Apollo. Bell was named the clearinghouse for all information and developed computer storage systems for this task. The Defense Metals Information Center at Battelle Memorial Institute, Columbus, Ohio, was invited to participate and to publish factual data to prevent misinformation concerning the nature of the progress.

Test Logic

With the problem definitely established as stress corrosion of the titanium with the N_2O_4, three approaches were established. The three approaches were: 1) to prevent, by means of platings and coatings, the titanium alloy from coming in contact with the corrosion fluid; 2) to change the stress, time, and temperature service environments sufficiently to prevent the problem; and 3) to add inhibitors or to remove contaminants from the N_2O_4 to avoid corrosion.

These approaches were dictated by the Project Apollo requirement that the titanium hardware in inventory had to be used with little or no modification, if at all possible. This requirement was necessary because of the cost involved, the long replacement time, and a prohibitive weight increase which would be caused by a change in the tank material. In addition, the change or modification had to be absolutely reliable for a man-rated spacecraft such as the Apollo vehicle.

Platings and Coatings

Three systems were evaluated in an effort to prevent contact between the N_2O_4 and the titanium wall. These were an oxide coating, an anodized coating, and a Teflon coating.

Oxide Coating. The investigators noted that the small Apollo tank differed from the other Apollo tanks in that the natural oxide formed during aging or stress relieving was removed from the lot of tanks which failed in N_2O_4, but was left intact on the previous successfully tested main propulsion tank. Several specimens and one tank were oxidized in air to form the tightly adhering blue oxides of titanium that usually are seen on heat-treated parts. These oxides are formed at temperatures from 1050° to 1200° F in air after a 1/2- to 1-hour exposure. Oxide-coated specimens failed with numerous stress-corrosion cracks even though electrical conductivity measurements indicated no break in the oxide coating. An RCS tank that was oxidized in air also failed during the test at approximately the same time as the tanks with bare surfaces; therefore, the oxide approach was abandoned.

Anodized Coating. The material supplier, TMCA, made provisions for anodizing several samples and two tanks at their Henderson, Nevada, facility. Anodized coatings were formed in a $NaNH_4HPO_4$ solution by a procedure developed by the Process Research Division of TMCA (6). This approach also was dropped because of the failure of the specimens and the failure of one of the tanks after a longer, but unacceptable, exposure to the N_2O_4.

Teflon Coating. Teflon is known to be permeable to N_2O_4, but at a relatively slow rate. Teflon is used as an inner container for a positive expulsion bladder in several Apollo applications and its inertness to N_2O_4 is well known. Early in the investigation, the use of Teflon was proposed and several samples of Teflon-coated titanium were tested. A properly coated specimen did not fail in test, but numerous difficulties in getting a defect-free coating left NASA with a low confidence in this approach for a man-rated system. For example, installation of fill and vent lines in a Teflon-coated tank could cause minute holes in the coating that were essentially not inspectable.

For these reasons, coatings could not be seriously considered as the primary, or sole, modification to the tanks to prevent the stress-corrosion problem. Plans to evaluate other coating systems such as aluminum or stainless-steel cladding required extensive development and did not appear to offer either an economical or a timely solution.

Modified Service Environment

As in other systems, the stress-corrosion rate in N_2O_4 is dependent upon the stress level, and the temperature of the metal and the corrosion fluid. For a given exposure time, stress corrosion can be avoided as a significant problem by lowering stress or temperature, or both. In the Apollo pressure-vessel application, the time under stress is dictated by the mission time, the wall stress is dictated by the system operating pressure, and the wall thicknesses depend upon the existing hardware. Temperatures can be lowered by loading the propellant cold (60° F) and maintaining the temperatures by insulation, thermal control coatings, and proper orientation of the spacecraft in flight. These measures are somewhat drastic in terms of mission restrictions, but nevertheless are considered possible. All of these data are based upon obtaining a reliable relationship of failure time versus temperature at a constant (worst case) stress.

Hundreds of specimens were tested in autoclave test cells at Bell, NAA, NASA Langley Research Center, and other installations. The results, along with several pressure-vessel tests, established a rather unreliable relationship which is shown in Fig. 5. The steep slope of the line in the figure makes the accurate prediction of the use temperature essential. These data for a vehicle going to or from the moon, or for a vehicle on the lunar surface, are not that accurate. NASA and the contractors decided that this approach could be used for insurance, but not as the primary solution to the problem.

It was stated earlier that the stress was fixed by wall thickness and operating pressure. However, the effective tensile stress could be lowered by surface treatments such as shot peening. Braski and Heimerl (7) have been working on shot peening of titanium to prevent stress corrosion in hot chlorides in support of the supersonic transport program. They directed their knowledge and support to the problem by utilizing glass-bead peening to introduce a residual compressive stress on the interior titanium surface. Personnel from Langley Research Center supplied several glass-bead peened specimens to Bell. (See Ref 7, pp. 1-3, for a description of the specimens.) These specimens were the first to give consistent, successful results. This approach was later scaled to tank size, and one of the Bell tanks successfully passed a 30-day test at 105° F at a 90-ksi wall stress. Several hundred samples were tested in autoclaves with complete success; therefore, shot peening was considered an acceptable means of modifying the Apollo hardware.

Modified Oxidizer Composition

Concurrent with the efforts described, a large effort was initiated to evaluate the trace elements in the N_2O_4. The investigators felt that the key to the test anomalies, such as the failure of some test centers to reproduce the stress corrosion under identical test conditions, lay in the trace contaminants present in, or in the actual composition of, the N_2O_4. The successful tank test in 1964 could be explained, in part, by the fact that the temperature may have been too low (60° to 80° F) to bring about failure within 30 days. However, later RCS tank tests (at NAA) at the controlled 105° F also did not fail. At this point, electron microprobe analysis, electron microscope fractography, and sophisticated laboratory analytical techniques were used to eliminate or isolate various suspect elements and compounds.

The approaches taken by NAA and Bell in the analyses of the N_2O_4 were quite different, yet led to identical conclusions. Since the N_2O_4 used at Bell resulted in repeated failures, Bell investigated the possibility of inadvertent contamination of the N_2O_4. Electron microprobe analyses showed some local concentrations of chlorine and iron near the fracture surfaces. Chlorine is known to cause stress corrosion of titanium, and efforts to produce chlorine-free N_2O_4 were undertaken at Bell. One approach was to precipitate the chlorine by adding an aqueous solution of silver nitrate to the N_2O_4. Using treated N_2O_4, the titanium did not stress corrode.

Meanwhile, at NAA, more than 300 titanium coupons were tested in N_2O_4 with no failures. Therefore, NAA considered they must be inadvertently inhibiting the N_2O_4 and sought to produce super-pure N_2O_4 by repeated drying, oxygenation, and distillation. Specimens tested in super-pure N_2O_4 failed. A review of the literature indicated that Rittenhouse (8) had stopped stress corrosion of titanium by the addition of nitric oxide (NO) in the fuming nitric acid system in 1959. Rocketdyne, Canoga Park, California, a division of NAA, was able to fail specimens consistently in N_2O_4, except for the specimens tested in N_2O_4 with high (above specification) water content. Since water was known to react with N_2O_4 and release NO, some insight into the cause of the stress corrosion was obtained. Bell tests confirmed that adding aqueous silver nitrate, aqueous HNO_3, or water to the N_2O_4 would inhibit the reaction. An exchange of N_2O_4 between Bell, NASA, NAA, and Hercules Powder Company, Wilmington, Delaware, revealed that the NO content of NAA propellant, though difficult to measure with existing analytical techniques at that time, was, nevertheless, significant. By cooling the oxidizer to 0° F, Bell demonstrated that the NAA oxidizer was green in color whereas the other oxidizers were yellow. The green color resulted from the mixture of N_2O_4 (yellow) and the dissolved inhibitor, NO, as N_2O_3 (blue). King, Kappelt, and Fields (9) provide a more detailed description of the chemistry involved. A retest was made of a main propulsion tank with uninhibited N_2O_4 to prove that previous successes with this tank were related solely to the NO content. The tank failed in 51 hours at 95° F.

Other investigators confirmed the correlation of test data with the NO content of the test fluid. It was found that if NO is present in the

N_2O_4 in measurable amounts, titanium alloys will not stress corrode. The reason early investigations showed the titanium to be compatible in N_2O_4 soon became evident, since prior to June 1964, N_2O_4, when manufactured, contained trace quantities of NO. In June 1964, an additional processing step was added to further purify the N_2O_4 and the trace NO was eliminated. Since the military specification on N_2O_4 does not require an analysis of NO, no clue was available at the start of the problem. Several tank tests of the inhibited N_2O_4 (N_2O_4 with NO present) were conducted at 105° and 165° F with no failures. Autoclave tests on coupons verified in large quantity that small additions of NO to the N_2O_4 would prevent stress corrosion of titanium. Therefore, a change to the N_2O_4 was acceptable for the Project Apollo modification.

Verification Test Program

NASA and the contractors had to decide which of the two solutions was the most reliable for a critical manned spacecraft application. The shot-peening process was subject to inspection difficulties. Further, the effect of localized surface damage (scratches) to the peened surface was unknown. The modification to the oxidizer composition was subject to questions concerning propulsion performance changes, stability, and analytical techniques. To answer some of these questions, an extensive verification plan was developed involving several full-scale tank tests.

Shot Peening

A process specification was written by representatives from NASA, NAA, Bell, and Grumman Aircraft Engineering Corporation, Bethpage, Long Island, New York. Arrangements were made to shot peen one of the main propulsion tanks at Langley Research Center. Photographs of the shot-peening process are found in Figs. 6 and 7. The tank used for this test was one that had been rejected for flight hardware because of several deformed areas in the cylindrical area. Although this condition was carefully examined by the investigators who felt that this deformation would not affect the test, subsequent testing in military-specification grade N_2O_4 resulted in failure, as shown in Fig. 8. Examination by the tank fabricator, Allison Division of General Motors Corporation, showed that local bending stresses around the deformation added to the hoop stress and left a net tensile stress high enough to cause stress corrosion in this area. No stress corrosion was found anywhere except in the deformed area, proving the effectiveness of the shot peening, but pointing out the absolute need for a lack of residual stress and for careful handling.

Modified Oxidizer Composition

Several hundred specimens tested in military-specification N_2O_4 with various amounts of NO added proved that stress corrosion of the titanium would not occur if the NO content exceeds 0.25% by weight. Due to the inaccuracies and the tolerances in existing methods of analyzing NO in small quantities, a minimum NO content of 0.4% by weight was established for the procurement specification. A NASA specification, MSC-PPD-2A dated June 1, 1966, "Propellant, Inhibited Nitrogen Tetroxide (0.40 to 0.80 Percent Nitric Oxide)" is presently in use to procure oxidizer for Apollo flights (Table 1).

A main propellant tank was tested for 80 days at 90° ± 8° F under maximum operating pressures with the NASA grade N_2O_4 and no problems were encountered. The tank was given a proof-pressure test at the end of the 30 days to demonstrate no degradation, prior to proceeding with the additional 50-day exposure. A significant problem was pointed out as a result of this approach: the analytical techniques for the procurement specification were reviewed and found to be inadequate. Considerable efforts were made to standardize the test techniques throughout the Project Apollo contractor system, and efforts are still underway to improve these analytical techniques by gas chromatography or nuclear magnetic-resonance techniques.

Conclusions

Based upon the success of the modified oxidizer and the shot-peening process problems, the Project Apollo will use the modified oxidizer to prevent stress corrosion of the titanium pressure vessels. One particular aspect of the problem which NASA is pursuing is to determine why the modification works. It is known that in the N_2O_4 system, dissolved oxygen is low when NO is present and high when NO is removed. Earlier work leads to the hypothesis that oxygen and chlorine are necessary for stress-corrosion cracking of titanium alloys in hot salt. The same requirements may be true here also. No real understanding of the inhibition of the corrosion mechanism is available at this time.

Another aspect of this problem pointed out that the compatibility tests and the compatibility data are only good for the precise conditions of the test. For example, a supposedly insignificant change in the manufacturing sequence of the N_2O_4 to improve the product voided all data on the titanium and N_2O_4 compatibility. In the case of the Project Apollo, a realistic component test revealed a problem that analysis, in lieu of tests, would not have shown. The compatibility data must be examined thoroughly to determine applicability; and for critical, man-rated components the data should be verified as carefully as possible using flight-environment simulation.

Acknowledgments

The authors wish to acknowledge the excellent work of Mr. R. E. O'Brien of North American Aviation, Inc.; Mr. C. E. Manning of the National Aeronautics and Space Administration, Langley Research Center; Messrs. C. Fields and T. Murphy of Titanium Metals Corporation of America; and Dr. W. Forgeng of the Union Carbide and Carbon Corporation in solving the problems described in this paper.

Table 1.- Composition of Nitrogen Tetroxide

	Percent required (by weight)	
	MIL-P-26539	MSC-PPD-2A
N_2O_4, min.	99.5	[a]98.70
H_2O, max.	.10	.10
Cl^- (as NOCl), max.	.08	.08
Nitric oxide (NO)	Not required	[a]0.6 ± 0.20
Particulate matter, max.	10 mg/l	10 mg/l

[a]The summation of N_2O_4 and NO will not be less than 99.5 percent by weight.

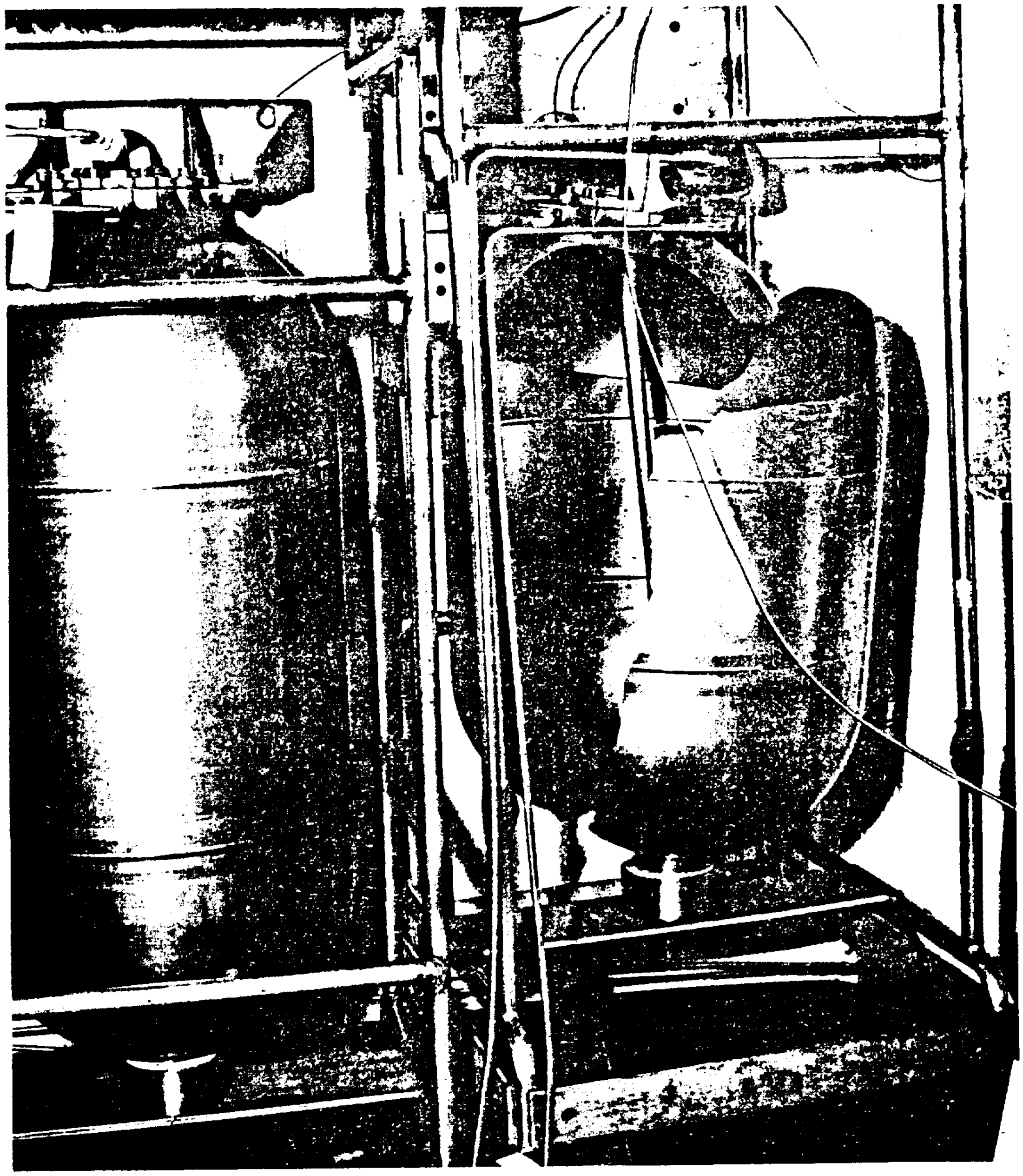


Fig. 1. Failed Apollo tank after a test of 34 hours in N_2O_4.

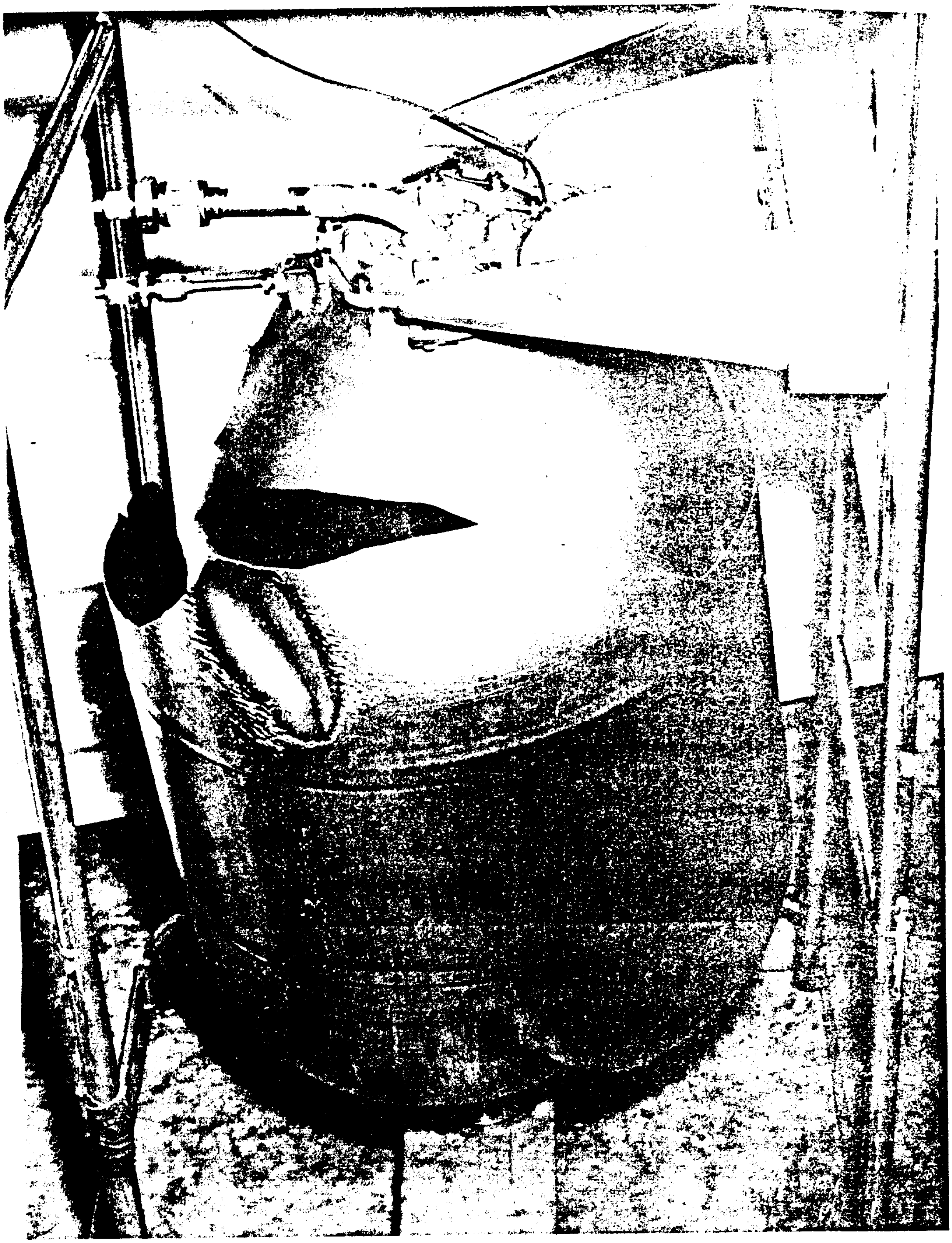
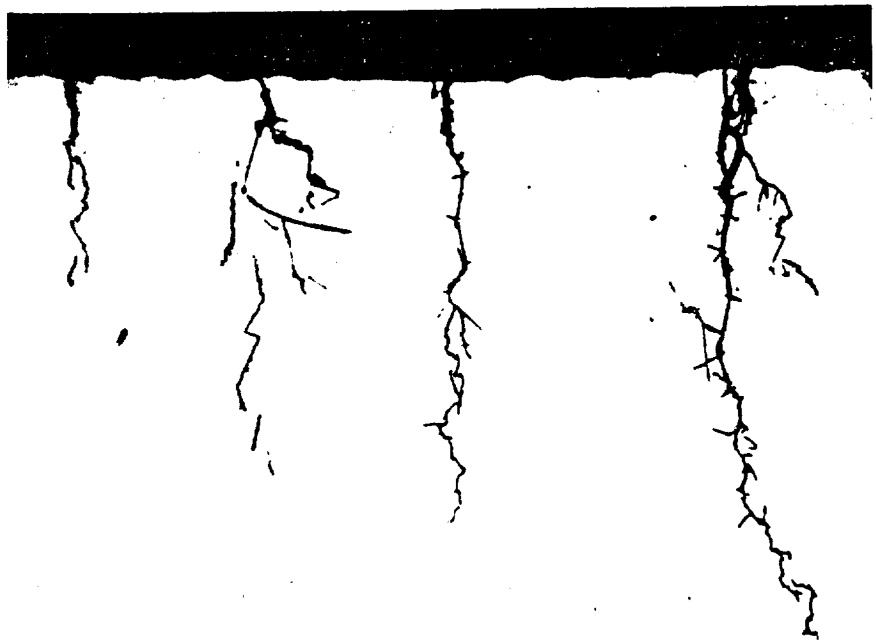
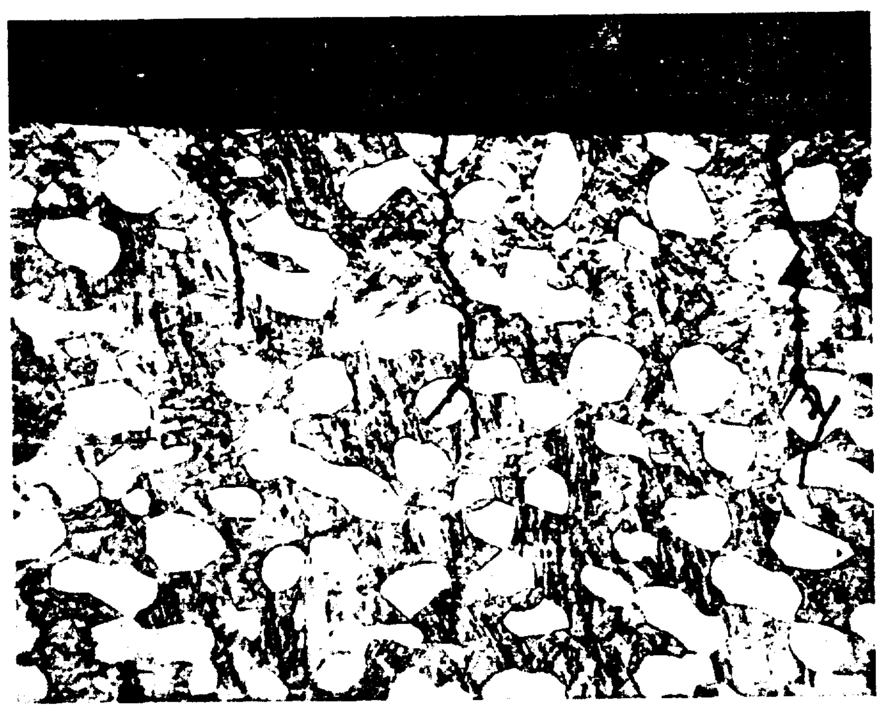


Fig. 2. Failed Apollo tank after a test of 34 hours in N_2O_4.



(a) Stress-corrosion cracks (X500).



(b) Stress-corrosion cracks (X750).

Fig. 3. Stress-corrosion cracks in 6Al-4V titanium after 34 hours in N_2O_4, 105° F, stress = 90 ksi.

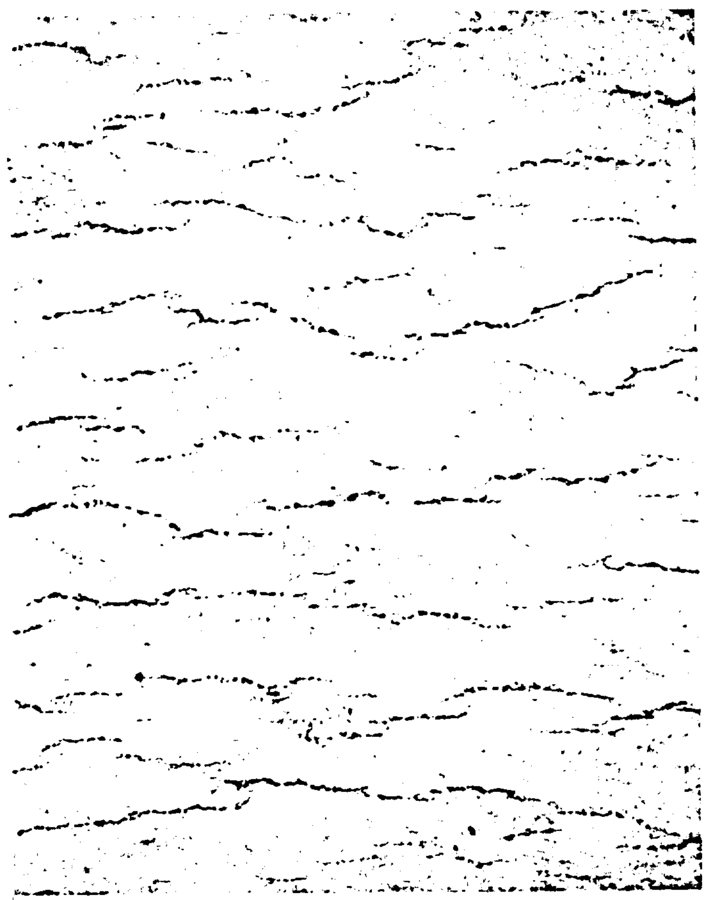


Fig. 4. Interior of tank in failed area (X100).

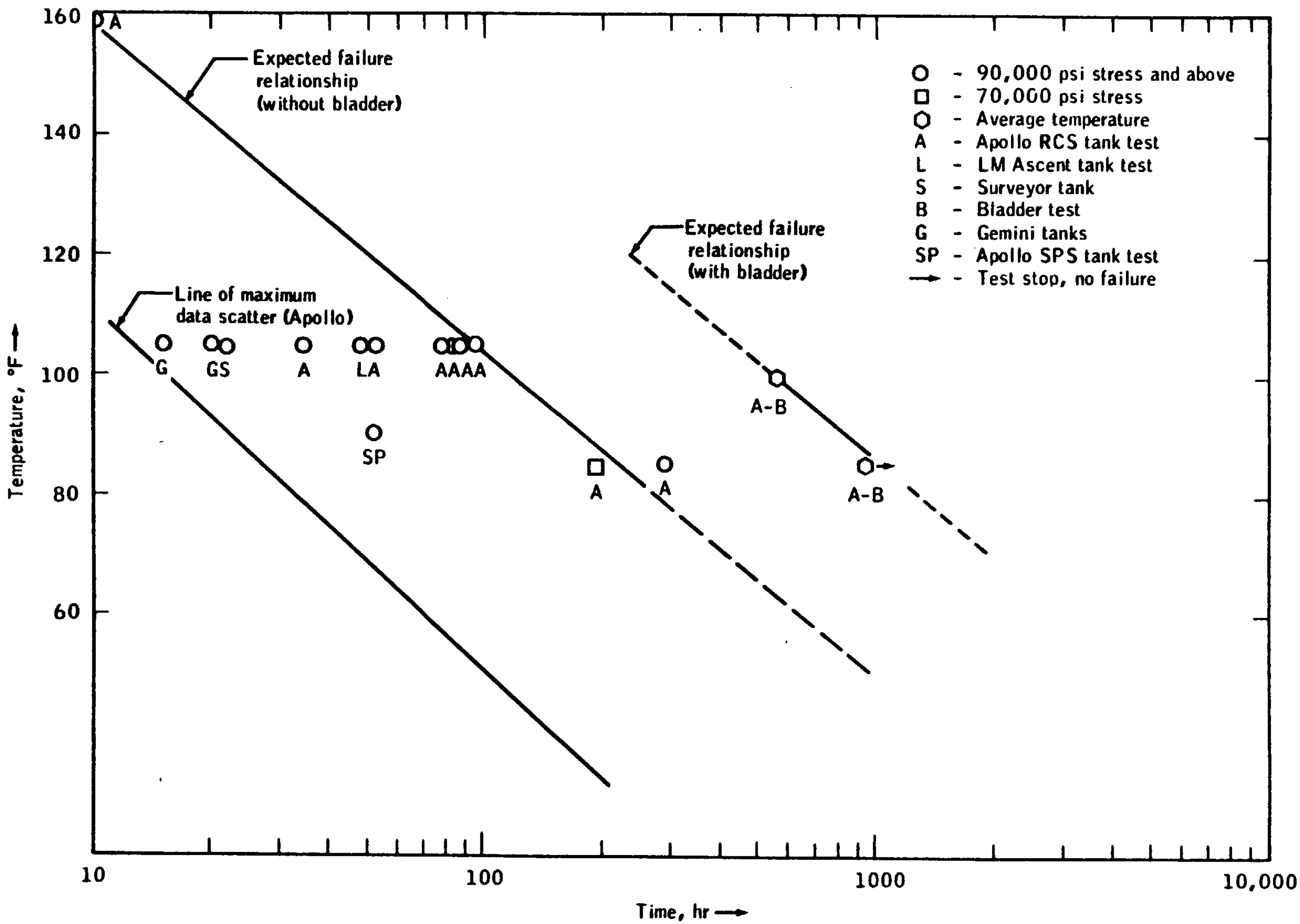


Fig. 5. Temperature versus time to failure for 6Al-4V titanium in N_2O_4.

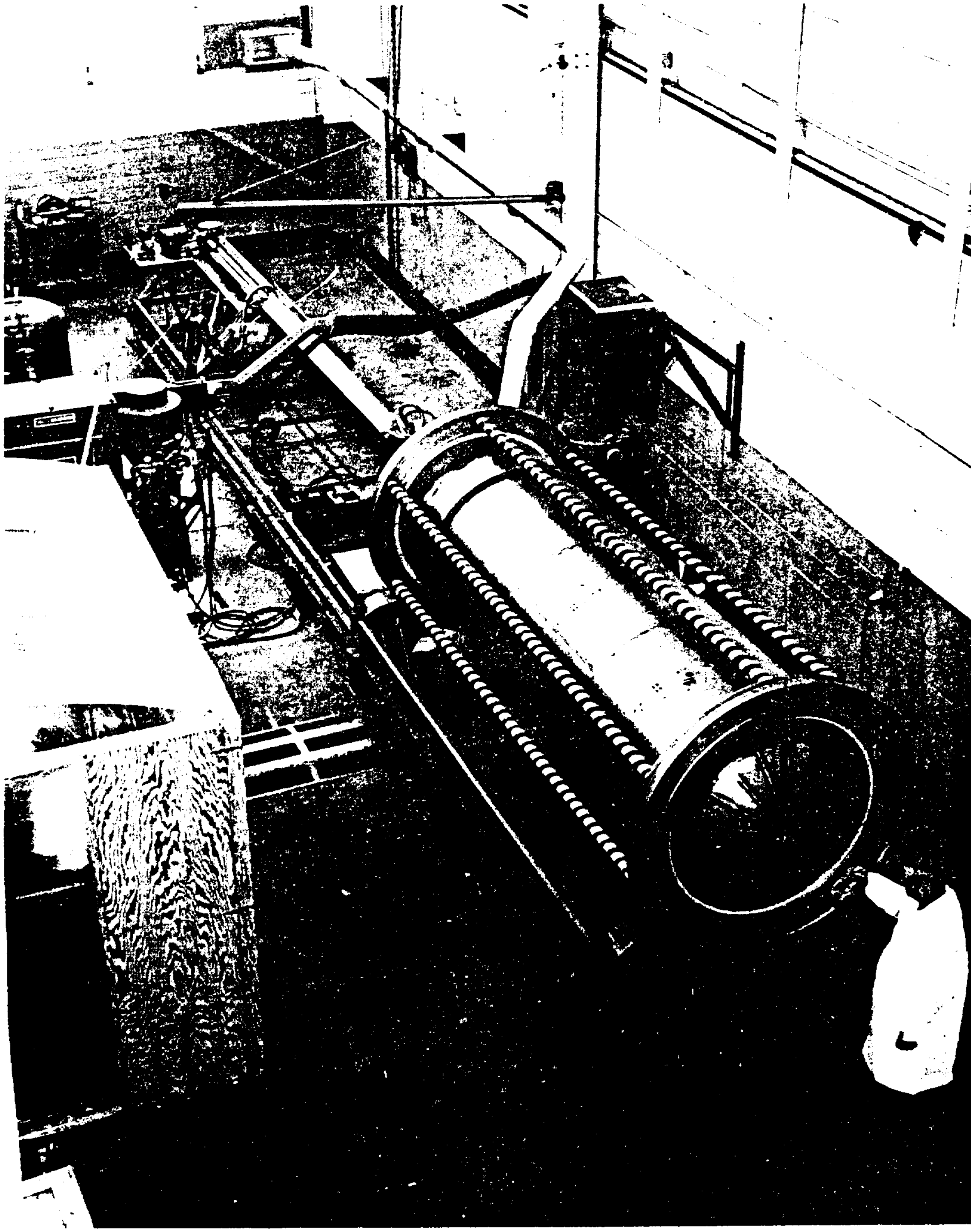


Fig. 6. Shot-peening process at Langley Research Center.

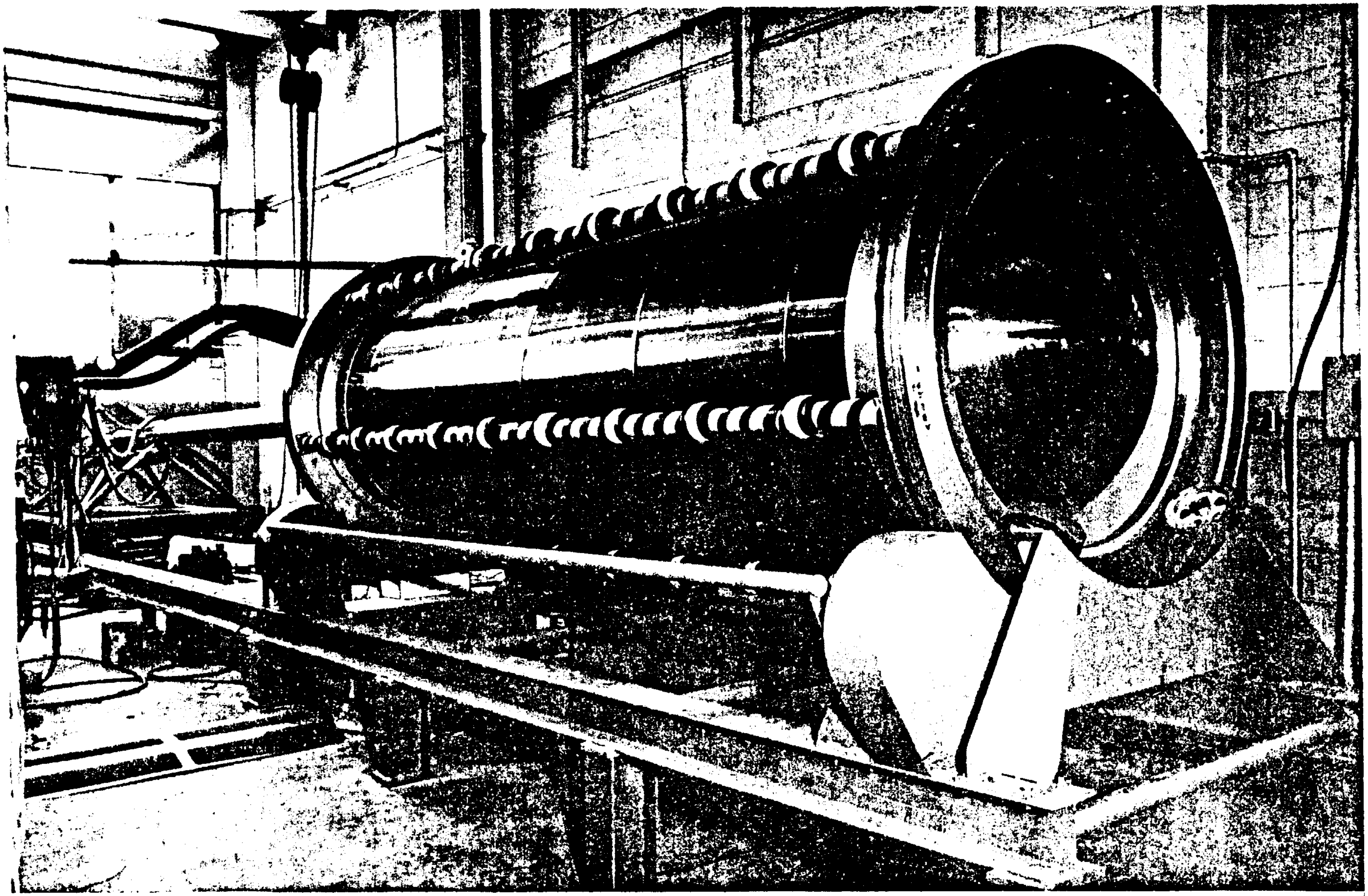


Fig. 7. Shot-peening process at Langley Research Center with the test tank in position.

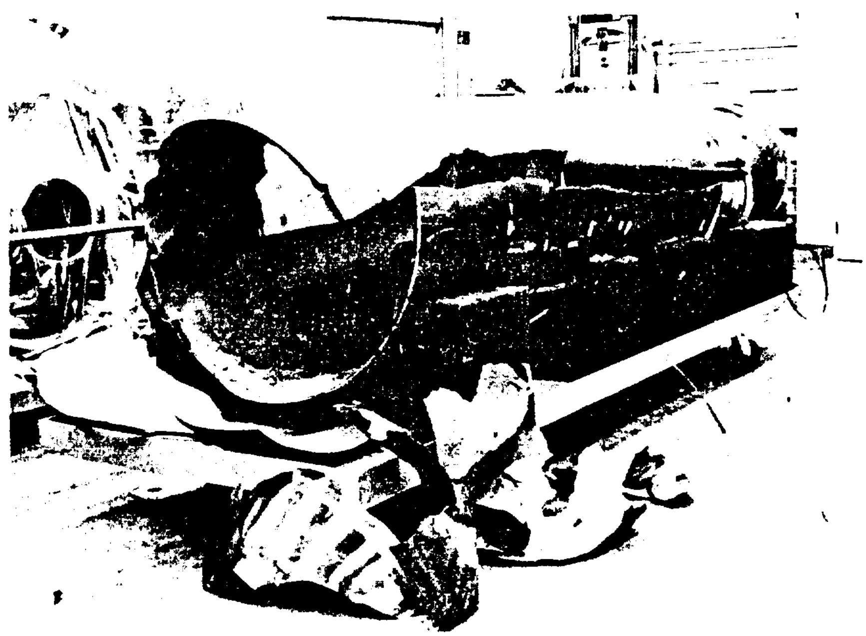


Fig. 8. Failed Apollo tank, shot peened at Langley Research Center, and tested by the Allison Division of General Motors Corporation at Wyle Laboratories.

REFERENCES

1. W. K. Boyd, Summary of Present Information on Impact Sensitivity of Titanium When Exposed to Various Oxidizers, Defense Metals Information Center Memo 89.

2. J. B. Rittenhouse, N. D. Stolica, S. P. Vango, J. S. Whittick and D. M. Mason, Corrosion and Ignition of Titanium Alloys in Fuming Nitric Acid, Jet Propulsion Laboratory, Contract AF-33(616)-3066, February 1957.

3. H. F. Scott, Jr. and C. W. Alley, Impact Sensitivity of Metals (Titanium) Exposed to Liquid Nitrogen Tetroxide, Wright Air Development Division, TR 61-175, May 1961.

4. C. W. Alley, A. W. Hayford and H. F. Scott, Jr., Nitrogen Tetroxide Corrosion Studies, Wright Air Development Division, TR 60-384, July 1960.

5. R. L. Wallner, Nitrogen Tetroxide Compatibility With Titanium Alloy 6Al-4V, North American Aviation, Inc., SDL 411, September 9, 1963.

6. L. C. Covington and E. E. Millaway, Anodization of Titanium in $NaNH_4HPO_4$ Solution, Titanium Metals Corporation of America, Henderson, Nevada, Project 47-42, Progress Report No. 4, September 1958.

7. David N. Braski and George J. Heimerl, The Relative Susceptibility of Four Commercial Alloys to Salt Stress Corrosion at 550° F, National Aeronautics and Space Administration, TN D-2011, December 1963.

8. J. B. Rittenhouse, The Corrosion, Pyrophoricity, and Stress Corrosion of Titanium Alloys in Fuming Nitric Acid, Trans. ASM, Vol 51, 1959, pp. 871-899.

9. E. J. King, G. F. Kappelt and C. Fields, Titanium Stress Corrosion Cracking in N_2O_4, National Association of Corrosion Engineers Conference Paper, Miami Beach, Florida, April 18, 1966.