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Prepared by J. K. STANLEY
Materials Sciences Laboratory

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Laboratory Operations
THE AEROSPACE CORPORATION

Prepared for SPACE AND MISSILE SYSTEMS ORGANIZATION
AIR FORCE SYSTEMS COMMAND
LOS ANGELES AIR FORCE STATION
Los Angeles, California

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FOREWORD

This report is published by The Aerospace Corporation, El Segundo, California, under Contract No. F04701-69-C-0066.

This report, which documents research carried out from July 1968 to July 1969, was submitted 29 September to Lieutenant Jerry J. Smith, SMTAE, for review and approval.

Approved

W. C. Riley, Director
Materials Sciences Laboratory

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

Jerry J. Smith
1st Lt., United States Air Force
Project Officer

ABSTRACT

In designing regeneratively cooled thrust chambers, the heat transfer conditions are selected to avoid "burnout" situations. Failure in engines using storable propellants during development, test, or operation seldom occurs by the burnout mechanism of design.

Roughening, pinholing, tube cracking, or splitting are common occurrences because of metal disintegration either on the combustion chamber side or internally within the tube due to two processes: (1) the combustion gases from nitrogen tetroxide and Aerozine-50 reacting with the stainless tubing (Type 347), and (2) the decomposition products of the Aerozine-50 degrading the interior of the tubes.

A mechanism of tube deterioration is developed to give a chronology of the events occurring from initial tube carburization to final tube failure.

CONTENTS

FIGURES

I. INTRODUCTION

Regeneratively cooled thrust chambers used for booster applications are made from thin wall tubing of Type 347 (18Cr, 8Ni + Cb) stainless steel. These tubes are about 1/2-in. diam with 12-to-16 mil-thick walls, and are brazed into an integral structure. In these regeneratively cooled engines, the cooling medium is the fuel that flows down one tube and up the other. These engines are designed to operate at around 760°C (1400°F) metal temperature in the throat area, which is the hottest zone of an operating engine.

In the type of deterioration discussed herein, the engine operates on storable propellants with nitrogen tetroxide being the oxidizer and Aerozine-50[1] being the fuel. The engine is designed on the basis of some fraction of the burnout criterion—that condition where the heat flux in the chamber can no longer be accommodated by fuel flow in the tubes. In such cases, the tube temperatures rise and the tube ruptures because of inadequate metal strength to accommodate the higher temperatures.

Data are presented to show that the primary failure mechanism is tube cracking or pinholing due to metal disintegration either on the combustion chamber side or internally within the tube. It has been established in our laboratory that failures seldom occur from loss of metal strength at high temperature. It has been shown that metal disintegration is caused primarily by carburization of external surfaces and carburization and nitriding of internal surfaces. These metal-gas reactions lead to some startling consequences.

Carburization is the metallurgical phenomenon by which carbon is introduced into the surface of a ferrous material by a diffusion process. The source of carbon can be a carbonaceous gaseous medium or a liquid, such as a cyanide. Nitriding is a similar phenomenon except, of course, that nitrogen is the diffusion specie.

[1] Aerozine - 50 is the trade name for a fuel consisting of 50/50 hydrazine (N_2H_4) and unsymmetrical dimethyl hydrazine ($N_2H_2(CH_3)_2$).

The nature of carburization is intimately related to the deterioration of this type of austenitic stainless steel. Some unappreciated consequences that result from carburization are: (1) loss of stainless quality of the steel,[2] (2) reduction of mechanical properties, and (3) under some conditions, loss of metal from the surface of the steel.

No attempt is made here to compare the carburization resistance of Type 347 stainless steels to other higher stainless alloy grades or superalloys. In petrochemical applications, where it has been necessary to reduce deterioration of steels by carburization, it has been possible to lessen this danger by increasing the chromium contents and/or nickel contents of the austenitic stainless steels. Stainless steels higher in alloy than Type 347 have not been used for aerospace applications. Where higher metal strengths at high temperature are required, superalloys have been used, e.g., Inconel X-750 in the F-1 engine.

[2] Aqueous corrosion and oxidation resistance are impaired.

II. LITERATURE

Although the literature on the elevated temperature deterioration of stainless steels in aerospace applications is virtually nonexistent, the nature of the attack, with respect to petrochemical applications, is documented. No references to deterioration of Type 347 in rocket engines were found. Although it is difficult to relate chemical plant deterioration at low temperatures, occurring over a period of years, to rocket engine failures, occurring at high temperatures in a few minutes, it is true that the failures have features in common.

Eberle and Wylie (Ref. 1) report severe metal loss with AISI Type 347 (18Cr, 8Ni + Cb) and Type 310 (25Cr, 20Ni) stainless steels used as structural material in a gas generator in which methane was burned with oxygen to form carbon monoxide and hydrogen for the Fischer - Tropsch synthesis. Loss of metal occurred between 480°C (900°F) and 900°C (1650°F). At the highest temperature, e.g., from 900°C (1650°F) to 980°C (1800°F), the steels became oxidized. Below 900°C (1650°F), heavy carburization occurred, interspersed with some oxidation. At lower temperatures, carburization and decarburization occurred alternately, depending on gas composition variations or temperature cycling.

X-ray diffraction analysis of the deposit revealed iron oxide, graphite, FeC, and metal particles.

The mechanism of "dusting" of the metal was probably caused by cyclic carburization followed by oxidation, facilitated by thermal stresses due to sootblowing (with steam) as well as by the abrasion of particles entrained in the gas stream. The brittle carbide layers appeared to flake off.

Metal loss by iron and nickel carbonyl formation was discounted because of the relatively high temperatures at which the failure occurred. Also, there was no noticeable change in surface nickel content.

Prange (Ref. 2) points out that the carburization of Type 310, Type 316 (19Cr, 8Ni, 2Mo), and Type302B (18Cr, 11Ni, 2-1/2Si) steels occurs at 600°C (1110°F) over a period of years but it does not cause plugging of the butane dehydrogenation unit. Other austenitic steels under similar conditions (Types 304, 321, and 347) produced considerable dusting or metal loss.

Hoyt and Caughey (Ref. 3) have found that Type 310 steel, operated 3000 hr at 650°C (1200°F) to 705°C (1300°F) and for one year at 480°C (900°F) to 540°C (1000°F), became heavily carburized. Type 302B (18Cr, 8Ni + Si) carburized slightly in 1700 hr at 480°C (900°F) to 540°C (1000°F). Carburization at these low temperatures was intergranular. The deterioration observed was nonuniform and took the form of pitting and general metal loss in the carburized area.

Lefrancois and Hoyt (Ref. 4) made an attempt in the laboratory to duplicate petroleum refinery metal loss in stainless steel grades. In Type 310, reactions were thermodynamically favored with CO, CH_4, and C in the range 370°C (700°F) to 815°C (1400°F). The carburized steel was found to contain two carbides, $M_{23}C_6$ and M_7C_3. Metal loss was explained by this sequence of events: Carbon enters the grain boundary as $Cr_{23}C_6$ and the grain boundary continues to grow. Then, the carbon diffuses into the matrix and carbides precipitate. There is an appreciable change in density, so much so that the grain is either disintegrated or lifts off from the steel matrix at the grain boundary.

Hockman and Burson (Ref. 5) have studied the deterioration of various metals including iron, iron-base alloys, and nickel in carbon monoxide, methane, and higher hydrocarbons. They have shown that dusting is related to the formation of carbides that decompose into iron and graphite. Most failures of heat-resistant alloys are associated with severe carburization. When these carburized alloys are exposed to an oxidizing environment, they are no longer as oxidation-resistant as they were before carburization. The type of high-temperature corrosion (which results in metal loss) in which the metal is first carburized and then oxidized, or is alternately carburized and oxidized, is also referred to as "green rot."

In Ref. 6 Schley and Bennett indicate that cast furnace tubes (30Cr, 20Ni, bal Fe) can fail in operation at 1100°C (2210°F) because of their high nitrogen content. Porosity and blisters can develop due to carburization and overheating. They point out that the carburized steel melts at about 1288°C (2350°F), whereas the HL alloy[3] melts at 1427°C (2600°F). When nitrogen has been sufficiently concentrated and/or the chromium content sufficiently depleted by carburization, the alloy becomes susceptible to blister or void formation because of the release of gaseous nitrogen.

[3] Heat resistant alloy casting containing 30% chromium, 20% nickel.

III. OBJECTIVES

The failure of regeneratively cooled rocket booster engines during development and testing prompted initiation of a study to explain reasons for the deterioration of thin wall tubes of AISI Type 347 stainless steel during engine operation with storable propellants.

Failure modes observed were pinholing, tube cracking and splitting, and roughening; laboratory experiments were conducted to determine possible causes of these failure modes. A microscopic examination of the tubes in the distressed areas of several engines was conducted to establish the type failure modes present.

After the failure modes were identified, they were verified through laboratory experiments.

A mechanism of tube deterioration was developed to provide a chronology of the events occurring in the chamber from the first signs of excessive heat flux (heat markings) to final failure.

IV. MATERIALS AND PROCEDURES

The aerospace industry initially selected Type 347 (columbium-stabilized) stainless steel over Type 321 (titanium-stabilized) for fabrication of thrust chambers because cleaner braze joints are possible with this material. The stabilized grades were preferred over Types 304 and 316 because of corrosion considerations.

Because brazing is an important operation in the fabrication of generatively cooled thrust chambers, a good wetting quality is essential in the material. A section of brazed tubes from a chamber is shown in Fig. 1 to illustrate the type of structure that is produced.[4] A complete engine of brazed-tube constructions, without its skirt extension, is shown in Fig. 2. Gold-base and maganese-base brazing alloys have been used successfully for joining these stainless steel tubes into an integral, gas-tight chamber.

A metallographic study was first carried out on some Type 347 tubes that were experimentally failed under burnout conditions, i.e., high heat flux conditions.[5] Such information was desired to determine if tube failures were indeed due to burnout conditions used as the basis for design of a rocket engine.

Metallographic studies were subsequently initiated to understand the nature of pinholes, cracks, roughening, and tube splits. In addition, carbon and nitrogen samples were studied using electron microprobe analysis.

Guided by the metal structures found in failed tubes from thrust chambers, carburization and nitriding experiments were performed to study structures developed under known conditions. Further, tube tensile specimens were carburized and tensile tests were run to study the effect of carburization on strength properties. Tube tensile specimens of nitrided stainless steel were also tested.

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[4] Heat markings below the bifurcated joint should be noted. Such heat markings also occur even in the absence of such construction.

[5] These samples were furnished by Dr. A. C. Kobayaski of Aerojet-General Corporation (Sacramento).

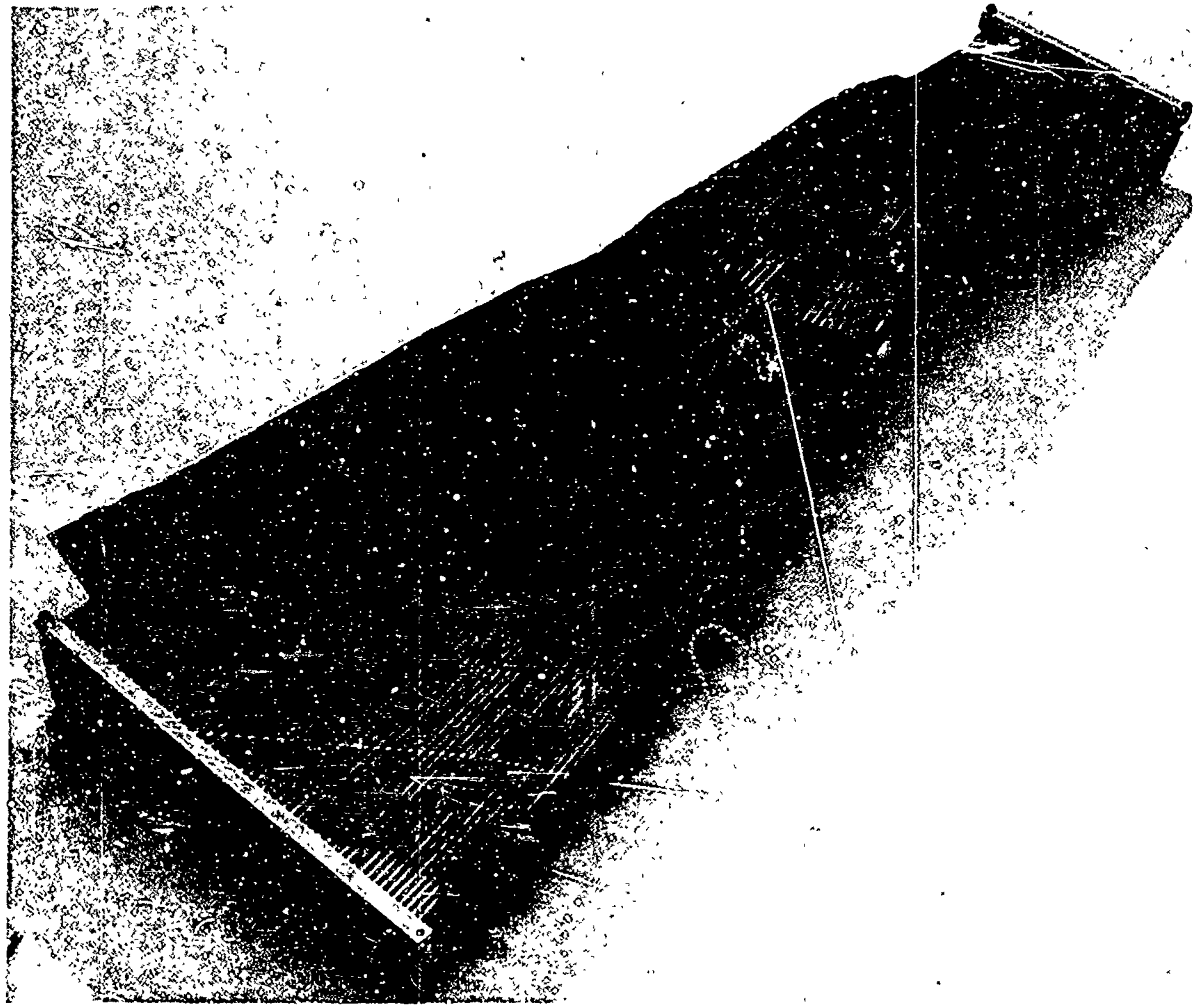


Figure 1. Rocket Engine Section Showing Brazed Tube Construction

(Terminal blocks installed for flow measurements; overall length about 5 ft. Note heat markings below the bifurcated joint.)

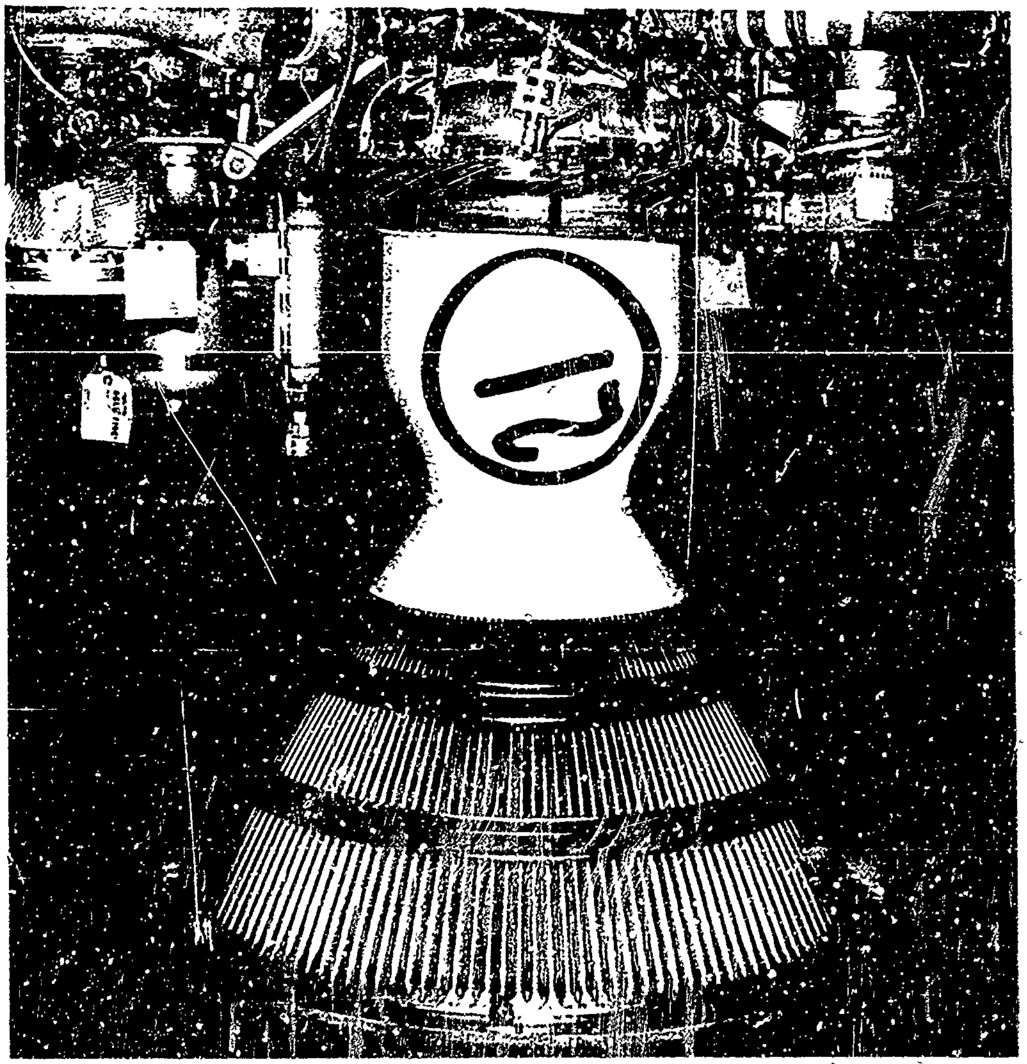


Figure 2. Complete Regeneratively Cooled Engine Without Skirt Extension

V. RESULTS

A. EXAMINATION OF BURNOUT SAMPLES

Burnout tests were conducted using electrically heated tube sections fabricated from Type 347 stainless steel. The test section was protected by a nitrogen atmosphere while Aerozine-50 circulated through the tube. The heat flux was increased stepwise until burnout failure of the tube occurred.

Figure 3 shows the nature of the failure of a Type 347 stainless steel tube under high heat flux conditions (16.88 Btu/in.^{2}-sec). Note slight flaring of the tube and carbonaceous deposit in the region of failure inside the tube. Flaring is caused by the biaxial stresses resulting from the internal pressure in the tube at the moment of rupture from high temperature. Carbonaceous deposit results from the decomposition of the Aerozine-50.

Photomicrograph Fig. 4(a) shows the coke formation and some carburization beneath the coking inside the tube in the vicinity of the failure (burnout); Fig. 4(b) shows the edge of the fracture and the voids show that the metal was separating at the increased temperature.

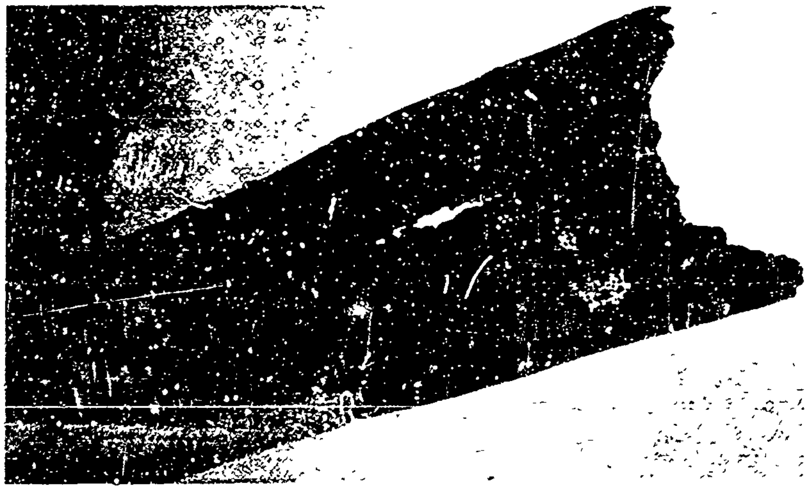
Figure 5(a) shows the microstructure in the vicinity of tube cracking. Wall thinning is probably explained by melting of the metal [1370°C (2500°F) to 1425°C (2600°F)]; Fig. 5(b) shows the resolidified steel (area with dendrites) adhering to the tube.

B. NATURE OF DETERIORATION

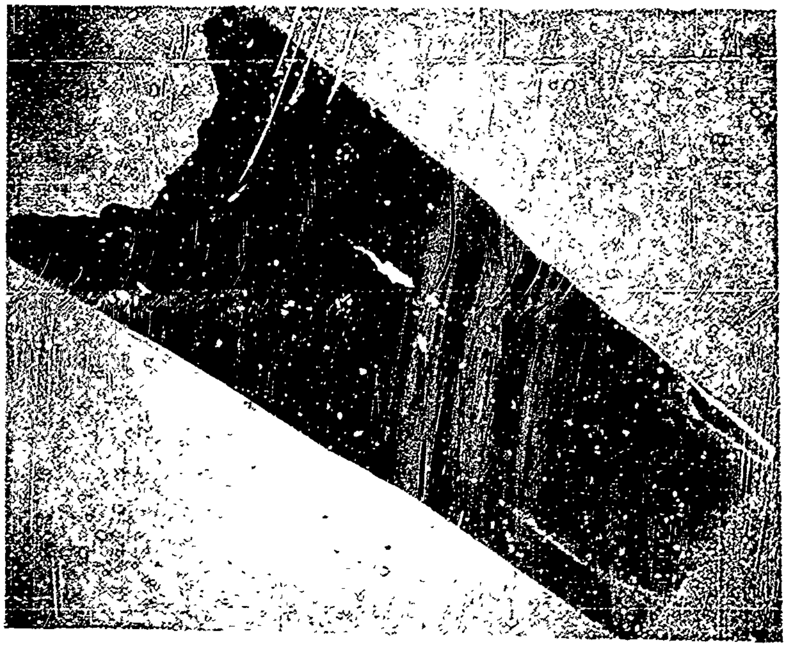
Five types of deterioration were observed on the brazed tube bundle on the chamber side of production engines: (1) heat-marking of certain tubes in chamber, (2) beads or crystallized material, (3) roughening, (4) pinholing, and (5) tube cracking.

1. HEAT-MARKING

"Heat-marking" is the term given to the discoloration of the Type 347 stainless steel tubing, usually located below the throat, that occurs in the thrust chamber. In regeneratively cooled thrust chambers, only isolated tubes,



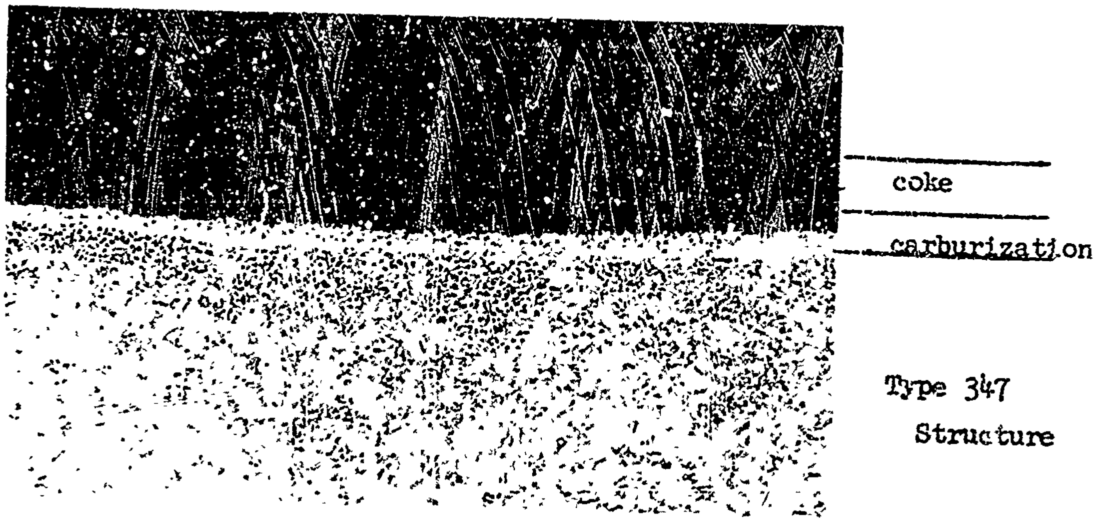
(a) External view 4X



(b) Internal view 4X

Figure 3. Failure of Type 347 Tubing Under Burnout Conditions

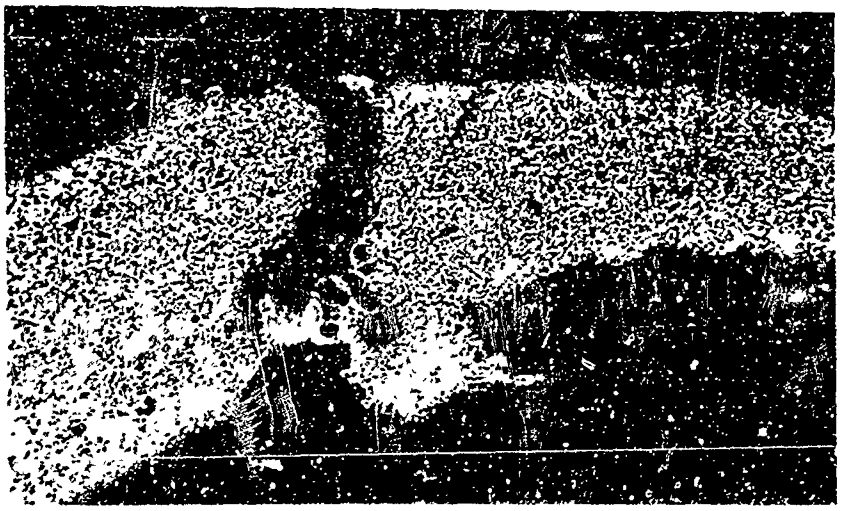
(Exterior blackening is oxide.)



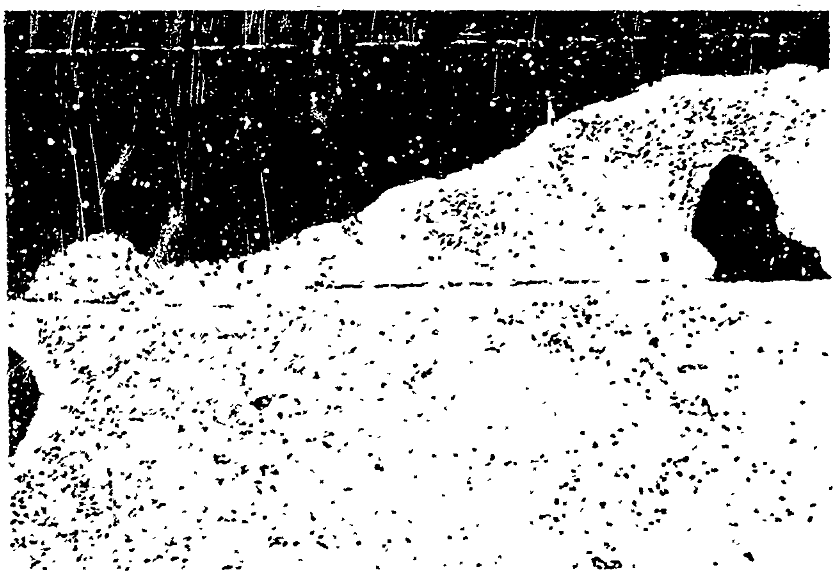
(a) Carbon deposits formed on inside of tube as a result of Aerozine-50 decomposition. 200 X

(b) Voids due to high temperature ruptures prior to complete tube separation. 200X

Figure 4. Edge of Fracture on Burnout Failure
(Etched in Aqua Regia)



(a) Cracking and wall thining in area of burnout 100X



(b) Areas of dendritic structures are resolidified metal adhering to wall 200X

Figure 5. Other Features at Edge of Failure on Burnout Sample

(Etched in Aqua Regia)

generally up-tubes, show heat-marking while adjacent tubes do not. However, by metallography, it is possible to show that in heat-marked tubes the structure is carburized and not oxidized. A polished but unetched stainless steel will reveal oxidation if it is present, but carbur ation is exposed only by etching. Figure 6 shows a section of a heat-marked tube. Note that on either side, the tubes are bright except for the splatter of resolidified braze alloy removed from between the tubes.

Carburization of Type 347 stainless steel only occurs above about 780°C (1530°F) (Ref. 7). Carburization at high temperatures can be quite rapid. As shown in Fig. 7(a) significant carburization of Type 347 can occur in 1 min at 1095°C (2000°F); Fig. 7(b) shows some of the carbide that has melted and resolidified (thin white layer). This is not an unreasonable temperature to be experienced by these tubes in this application. Note coarse grain size in Fig. 8, which attests to this temperature range. Also note the carburized (mottled) layer on the tube.

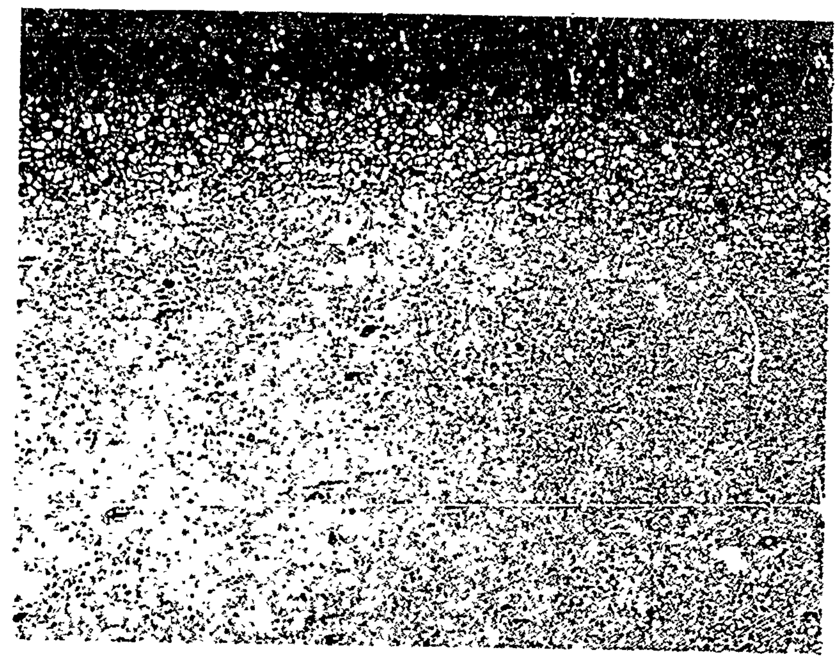
Examination of the back side of the heat-marked tubes reveals "soot" deposits [Fig. 3(b)]. As temperature excursions above about 300°C (575°F) are made, nucleate, and eventually, film boiling occurs in the Aerozine-50. Because of the high temperature, some of the coolant decomposes and reacts with the tube wall and a carbonaceous deposit forms. X-ray analysis identified the "soot" as a Cr_7C_3 carbide; some amorphous carbon apparently is also present.

2. BEADED OR CRYSTALLIZED MATERIAL

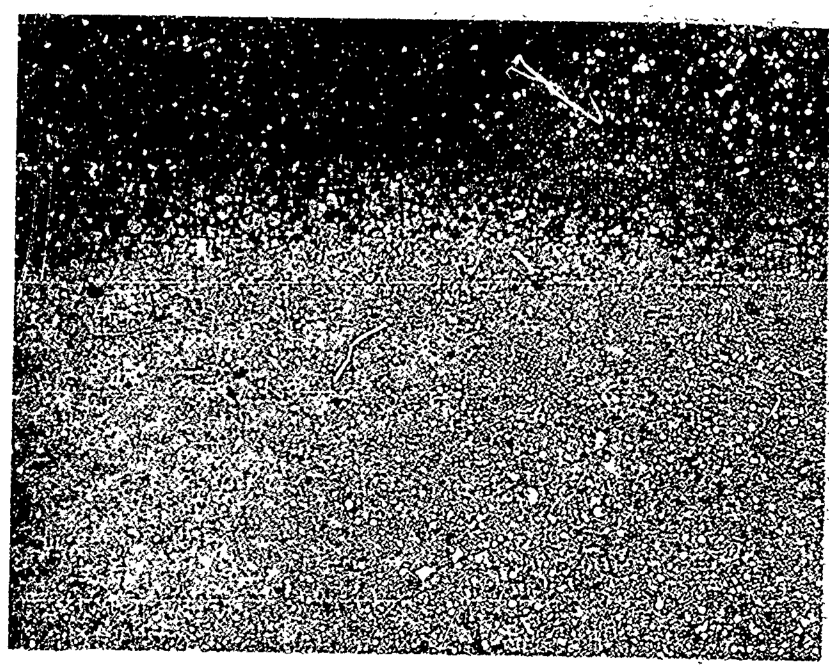
Occasionally, solidified beads or crystallized metal, apparently melted from the tubes, appeared on the combustion side of the chamber. Figure 9(a) shows a beaded spray and Fig. 9(b) shows the crystallized metal. This material had been assumed to be molten metal, but x-ray analysis identified it as a Cr_7C_3 carbide.

Various melting temperatures were observed for this carbide; some as low as 1095°C (2000°F) and some as high as 1260°C (3200°F). This variation in melting temperature is probably due to different carbon contents in the carbide.

Figure 5. Heat Marked (Black) Tube in Vicinity of Bright Tubes 8X

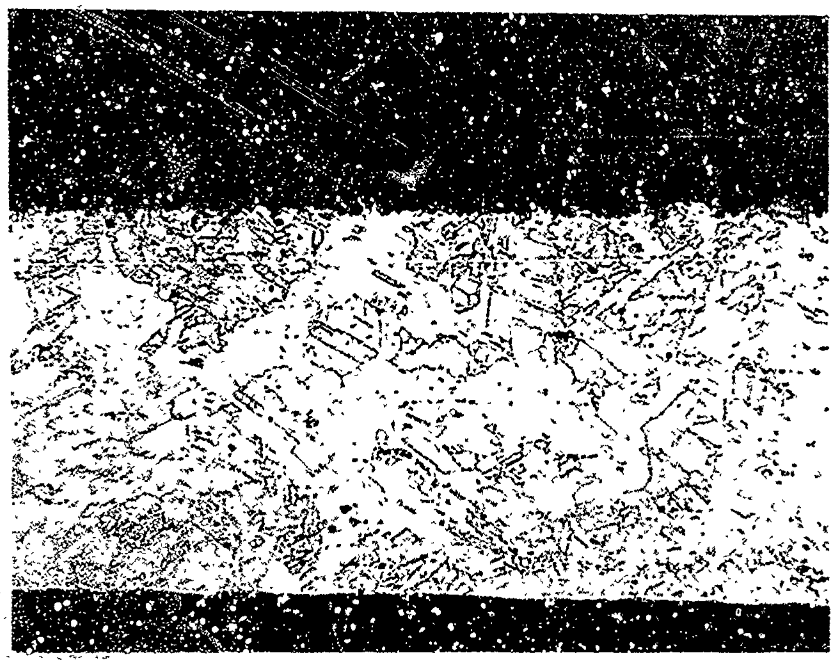


(a) Carburized 1 min @ 1095°C (2000°F)



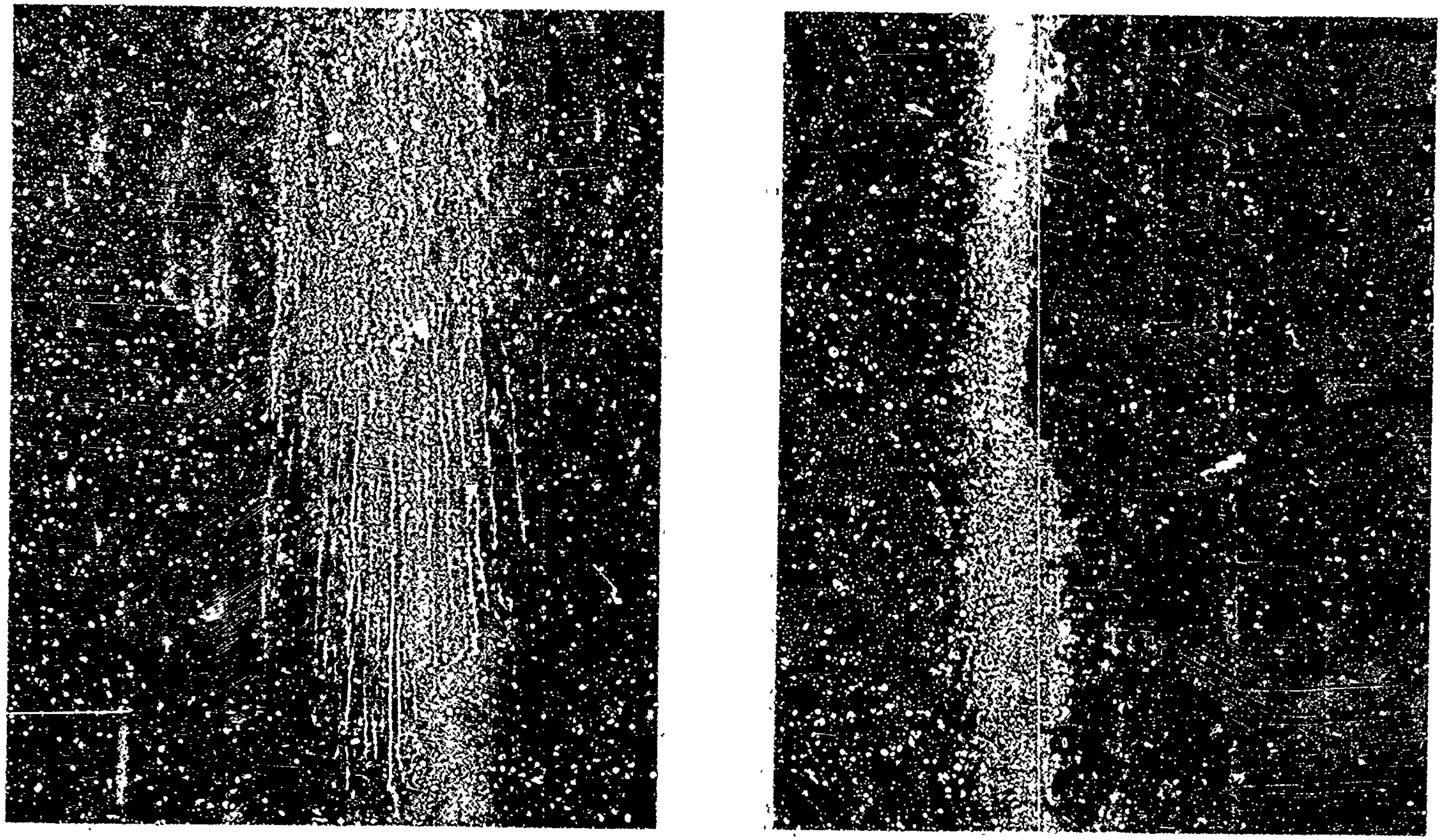
(b) Carburized 1 min @ 1120°C (2250°F)

Figure 7. Micrographs of Rapidly Carburized Type 347 Stainless Steel



Etched in Aqua Regia 100X

Figure 8. Micrograph of Heat Marked Tube
(Black lines above and below micrograph are separations between steel and mounting medium.)



(a) Beaded spray 4X

(b) Crystallized material 4X

Figure 9. Two Types of Deposits Found on Type 347 Thrust Chamber Tubes (Both are a carbide, Cr_7C_3)

3. ROUGHENING

Roughening of tube material often occurred. Roughening due to the resolidification of remelted braze material was referred to earlier (Fig. 8). Roughening, representing metal loss, was often found in association with pinholes and cracks.

4. PINHOLES

Pinholes (Fig. 10) are perforations of the tube wall. The holes always appeared in a roughened area, often in association with cracks.

5. TUBE CRACKING

Tube cracking, sometimes transverse and sometimes longitudinal, was often observed in tubes subjected to high temperatures (Fig. 11). Longitudinal cracks, when they penetrate the wall, are called "splits."

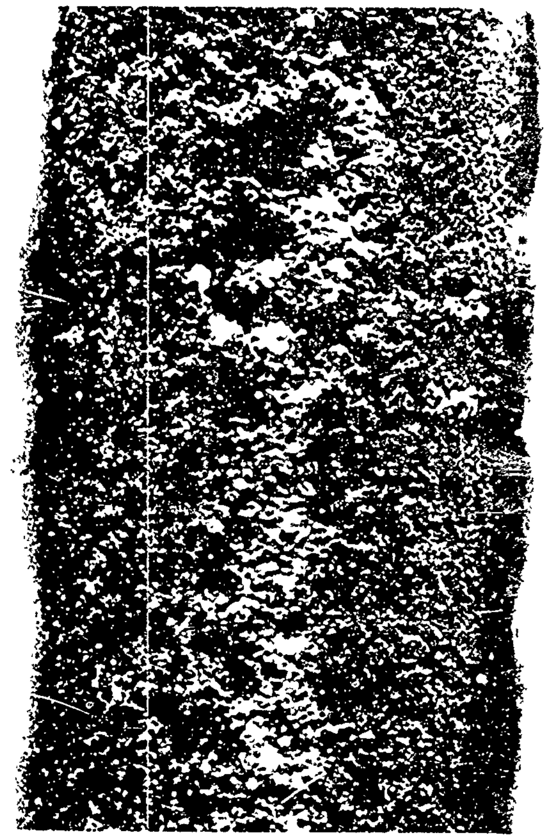
C. MICROSCOPIC EXAMINATION OF THE DISTRESSED AREA

Metallographic studies of the distressed tubes were undertaken in order to arrive at some mechanism of the failure modes mentioned. Upon examining the microstructure it was immediately obvious that metal deterioration was occurring from both outside and inside the tubes.

Sections through pinholes and cracks showed carburization on the outside and carburization and nitriding on the inside of the stainless tubes. Sometimes, only carburization was observed inside the tubes, according to microprobe analysis. In addition to the carburization and nitriding, there was evidence of metal loss both inside and outside the tubes, causing thinning of the tube walls. Metal loss mechanisms on either side were probably of different types. Obviously, as wall thinning proceeds, tube failures occur due to roughness, perforations, cracks, and splits.

The microstructure in the vicinity of cracks is shown in Fig. 12. Note carburization (black areas) on the external surface, and cracks in the carburized layer. Note the carburized (black) and the nitrided (white) zones on the internal surface, and the cracks on the internal surface. Severe metal loss on the

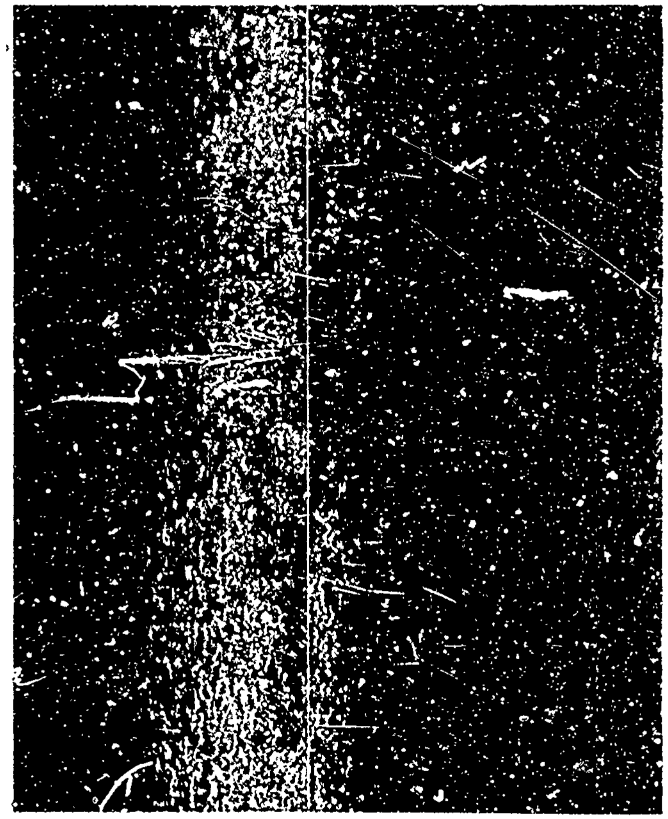
(a) 4X



(b) 4X

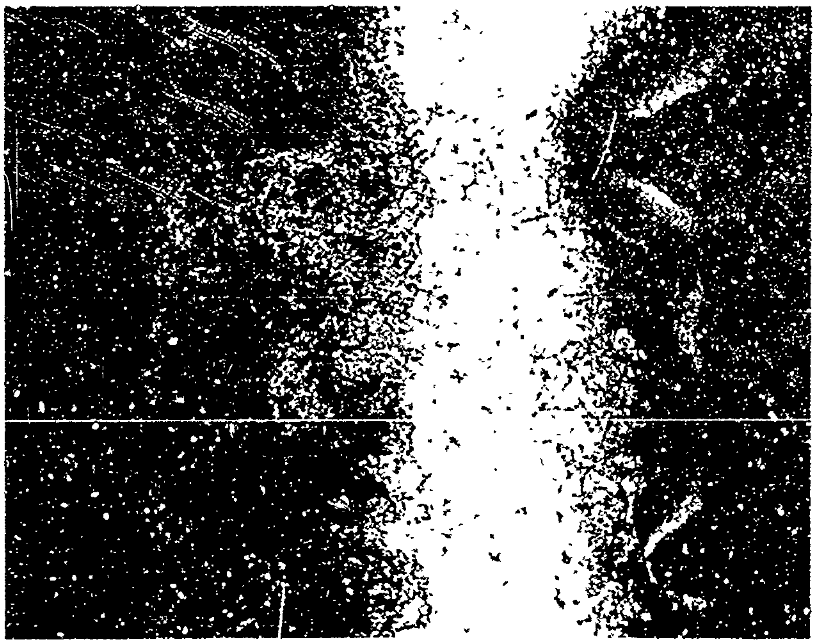
Figure 10. Pinholes and Associated Roughness in Type 347 Tube Bundle

(a) About 6X



(b) About 5X

Figure 11. Examples of Transverse and Logitudinal Cracking Observed on Distressed Tubes



(a) 200X

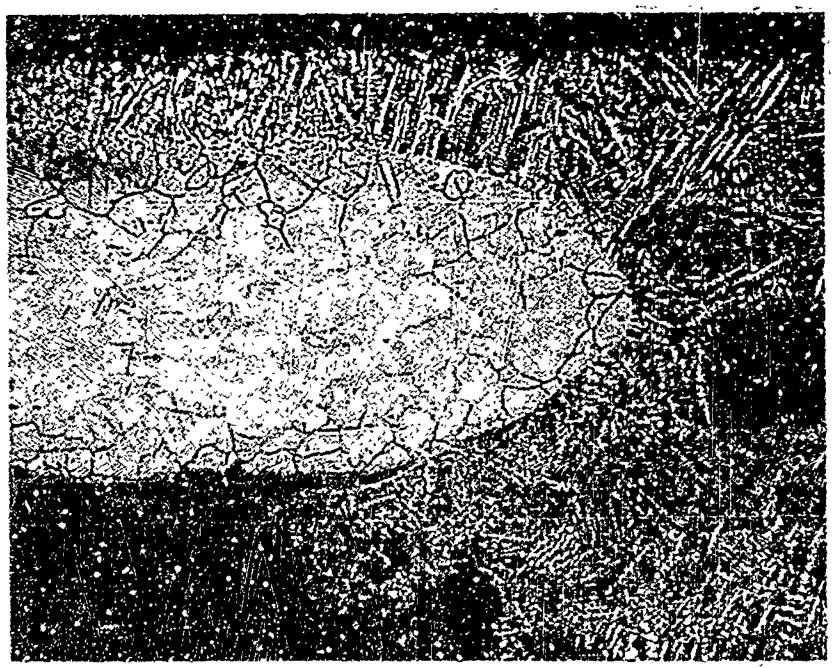
(b) 200X

Figure 12. Microstructure of Distressed Type 347 Stainless Steel Tubes Etched in Aqua Regia

internal surface is shown in Fig. 13(a). Occasional melting can occur as shown in Fig. 13(b).

A microprobe traverse was made on the distressed tubes to identify the carburized and nitrided zones (Fig. 14).

(a) Etched in Aqua Regia 100X



(b) Etched in Oxalic Acid (Electrolytic) 100X

Figure 13. Microstructure of Distressed Type 347 Stainless Steel Tubes Etched in Aqua Regia and Oxalic Acid

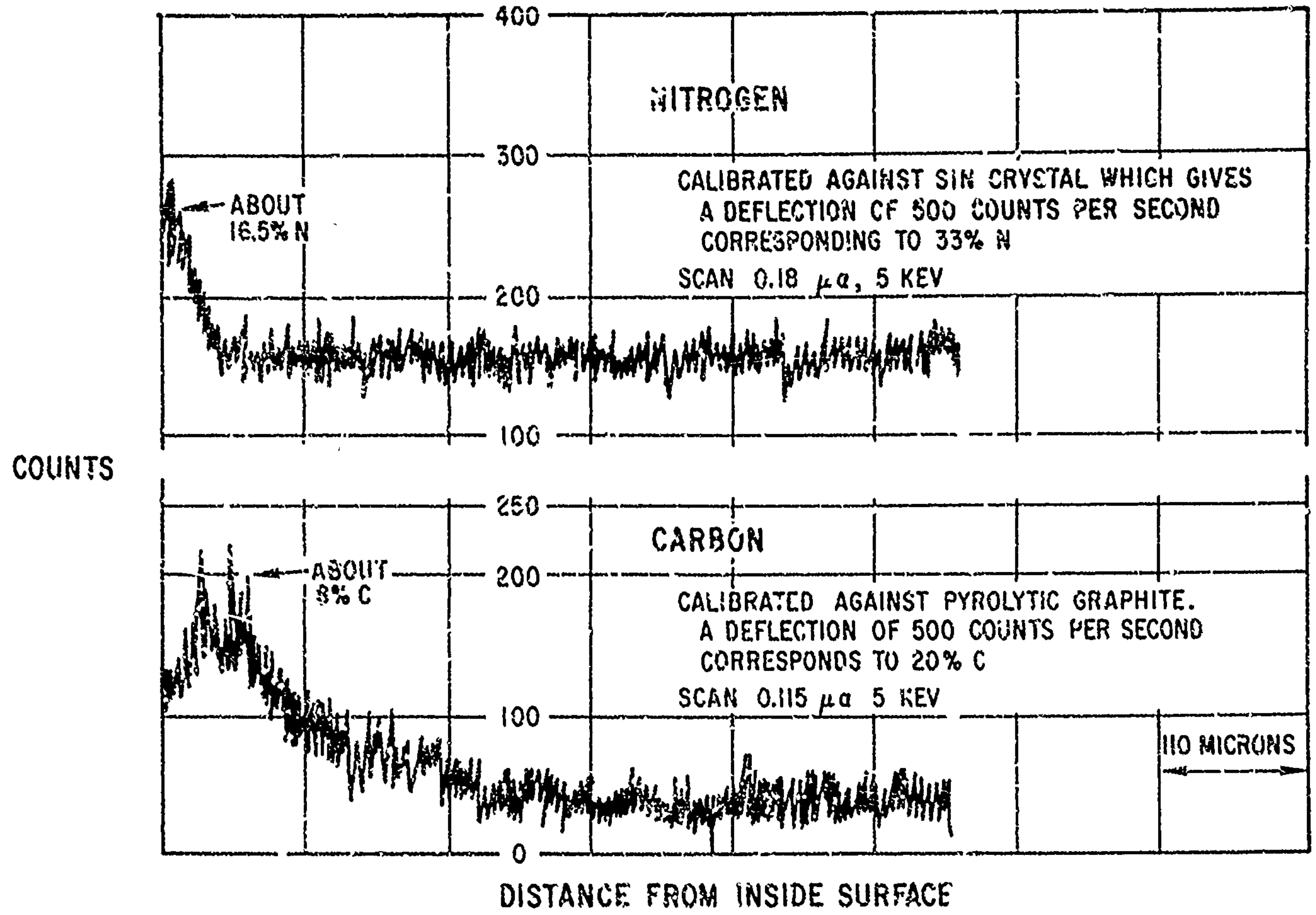


Figure 14. Microprobe Traverse on Inside of Distressed Type 347 Stainless Steel Tube

VI. DISCUSSION

The phenomena that can be considered in explaining deterioration of stainless steel tubes in thrust engines include: (1) burnout; (2) external carburization, including loss of ductility and low-melting carbide; and (3) internal carburization and nitriding.

A. BURNOUT

In the idealized heat transfer situation, when the coolant (fuel) in the tubes can no longer carry the imposed heat flux, the tube temperature increases. Nucleate boiling, and later film boiling, occurs (Refs. 8 and 9). In later stages of film boiling, the metal temperature increases rapidly and can approach the melting point. Before the melting point is reached, the strength of the metal is decreased to such an extent that the hydrostatic pressure of the coolant deforms and may rupture the tubes. None of our failed engines indicated this type of structure, which may be referred to as a classical burnout.

B. EXTERNAL CARBURIZATION

External carburization occurs as a result of the combustion of the nitrogen tetroxide and Aerozine-50. Film cooling (fuel) is also used to protect the stainless steel injector (also Type 347). The film cooling causes carburization of the chamber tubes. Virtually no oxidation occurs except when wide variations exist in the mixture ratio or in cases of insufficient film cooling.

Heat-marking is the first sign of carburization. The color of this heat marked area does not change as carburization proceeds inward, although the size of the carburized area can increase longitudinally.

One unfortunate consequence of carburization in Type 347 stainless steel is the loss of ductility (Ref. 10). See Fig. 15. Figure 16 shows the cracking that develops when a carburized steel is pulled in tension. The specimen was originally carburized in 1-1/2 vol % methane in hyrogen for 1 hr at 980°C

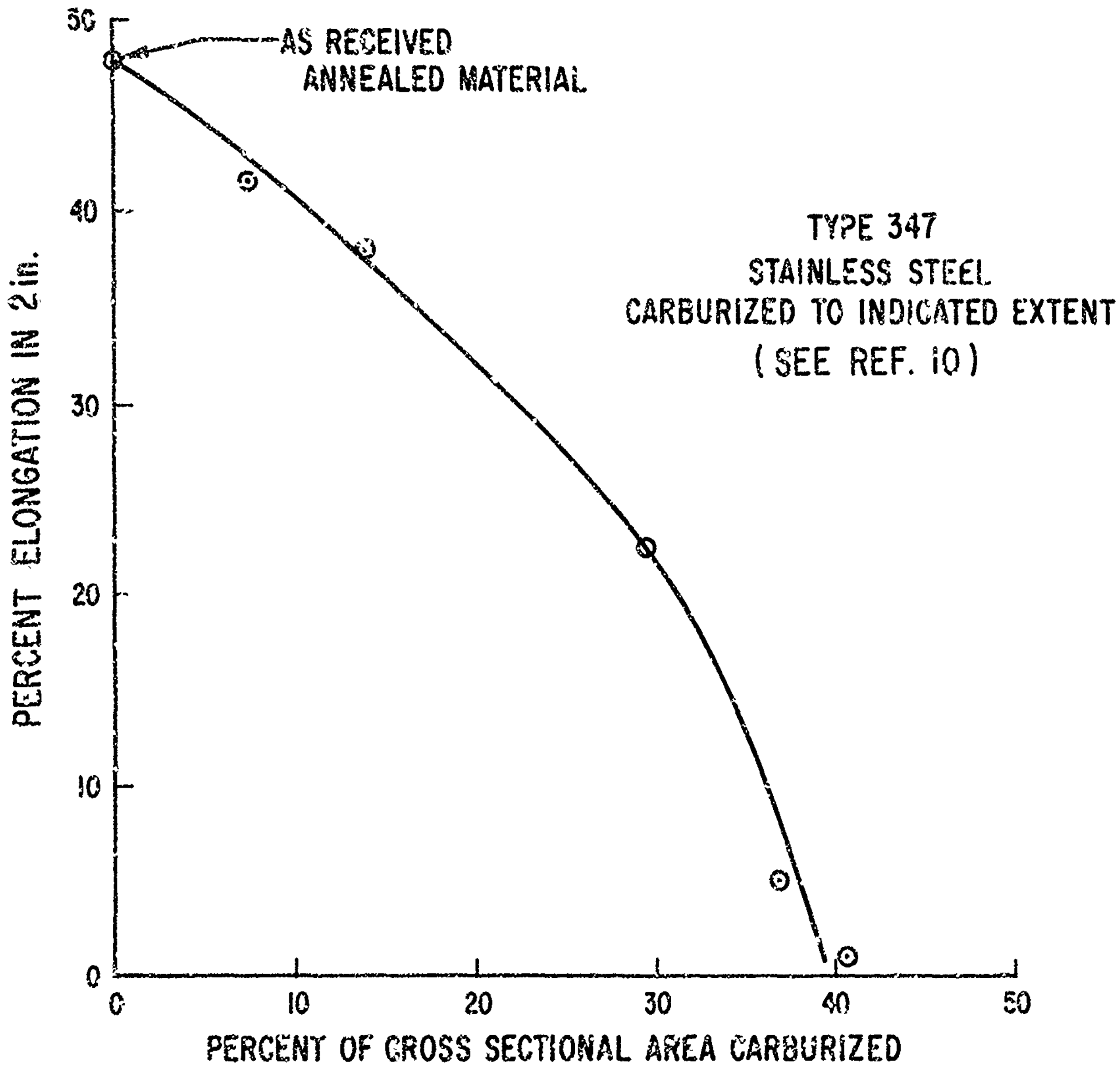


Figure 15. Decrease in Ductility in Relation to Carburization in Type 347 Stainless Steel

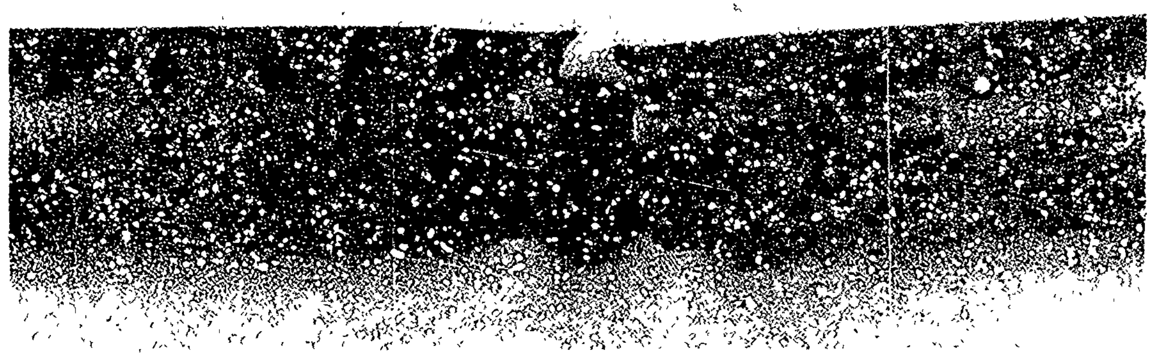


Figure 16. Cracking of Carburized Type 347 Stainless Steel Tubing Tested in Tension

(1800°F). The formation of a nitride case decreases the ductility of the Type 347 steel even more than does the carburization (Ref. 11). Similar cracking occurs.

During firing and refiring, the chamber undergoes considerable dimensional change, and superimposed on these changes is the stress from the biaxial mode from the coolants. Hence, if there is limited ductility in the carburized and/or nitrided steel, cracks develop. The nature of the cracks (transverse or longitudinal) is determined by the type of stress that predominates.

If the temperature in the thrust chamber increases to about 1095°C (2000°F) or higher, the carbide melts and may be blown out of the engine in the high-pressure gas stream. See Fig. 7(b).

C. INTERNAL CARBURIZATION AND NITRIDING

Microprobe and metallographic analyses indicated two zones on the inside surface of the stainless steel tubes - a dark etching carburized structure consisting of carbide ($Fe\cdot Cr_7C_3$) and austenite, and a light etching constituent, superimposed on the carburized layer, consisting of nitride $(Fe\cdot Cr)N$.

The carbide, because of its extensiveness, and probably to some extent the nitride, decrease the ductility of the steel and cracks develop due to dimensional changes in the chamber resulting from thermal transients. In addition, large areas where metal is dislodged from the distressed area appear.

With the information obtained from the examination of the distressed stainless tubes of regeneratively cooled thrust chambers using Aerozine-50 and nitrogen tetroxide, some ideas on mechanisms of deterioration of the tubes can be postulated.

Of several thrust chambers examined, no evidence exists of classical burnout where the heat flux is so high that the tube temperature increases and the tube merely ruptures due to the biaxial stresses in the tube.

Failure mechanisms observed are related to the actual deterioration of the stainless steel tubing. Gas-metal reactions occur that cause not only loss of ductility of the steel, but also loss of metal on the exterior and interior of the tubes, and finally in structural failure of the thinned and weakened tubes.

Some details of the total picture may still be missing, but the outlines of circumstances leading to embrittlement, wall thinning, and finally cracking or pinholing can be given.

For reasons not well understood, the flow rate of the coolant fuel in certain tubes, generally the up-tubes, of an operating engine sometimes diminishes unpredictably. This decrease in flow rate affects the heat transfer from the combustion side of the tubes and the tube starts to run "hot". As mentioned earlier, the first visible signs of hot spots are heat marks, or carburized areas. This effect is strangely localized; adjacent tubes may remain unaffected, i. e., bright in appearance.

Because heat-marking occurs at or above about 780°C (1530°F), the tube is operating above its design temperature. "Soot" deposits appear on the internal wall of the tubes, indicating that film boiling has occurred and that the coolant has decomposed. The increasing temperature causes the Aerozine-50 to decompose. The unsymmetrical dimethyl hydrazine, being less stable than the hydrazine fraction, decomposes first and the methane immediately carburizes the stainless steel as follows:

$$3N_2H_2\,(CH_3)_2 \longrightarrow 3N_2 + 6\,CH_4$$

or

$$3N_2H_2\,(CH_3)_2 \longrightarrow N_2H_4 + 2N_2 + 2CH_4$$

Thereafter, the hydrazine fraction decomposes as follows:

$$3N_2H_4 \longrightarrow 2NH_3 + 2N_2$$

$$NH_3 \longrightarrow N_2 + 3H_2$$

Nitrogen from any of the above reactions may cause nitriding. A white nitrogen layer appears on the inner surface of the tube wall, obviously at some-time after intensive carburization.

Because the film boiling that occurs inside the tubes cannot remove heat fast enough, the temperature continues to rise, thus increasing tube damage.

As temperatures increase above 1095°C (2000°F), more carburization occurs inside and outside the tube. Thermal and biaxial stresses occur simultaneously and since the carburized tubes have limited ductility, they crack externally and internally. Crack surfaces also carburize, weakening the structure further.

As the temperature increases, the surface carbide melts and is blown away, resulting in surface roughening. When this molten metal is blown out, the tube walls become thin and less capable of withstanding the combined stresses. Some carbon, of course, continues to diffuse into the steel. Conceivably, existing cracks can propogate more easily under such conditions.

Carburization of internal surfaces also continues. New carbon is deposited from vapors and gases and previously deposited carbon continues to diffuse. As all the carbon diffuses, the surfaces become brittle.

Another unfortunate consequence of this carburization and nitriding is that the alloy becomes susceptible to blister and void formation when the chromium content of the steel has been depleted by the carburization and nitriding processes. The removal of chromium from the austenite by carbon favors the release of gaseous nitrogen from the low chromium austenite (Ref. 6). Release of nitrogen gas could well displace the brittle carbide and nitride layers. The removal of the carburized and/or nitrided internal layers would also be a metal removal process.

Eventually, a puncture or pinhole occurs in a cracked area or where the metal has been severely thinned. This thinning is not always a uniform process; in regions where greater thinning occurs, vertical rupture cracks can appear.

VII. CONCLUSIONS

Brazed tube, regeneratively cooled thrust chambers using storable liquids (nitrogen tetroxide and Aerozine-50) seldom crack under classical burnout conditions. Observed failure mechanisms are related to the actual deterioration of the stainless steel tubing. Gas-metal reactions (i.e., carburization and nitriding) occur that not only cause loss of ductility of the steel but also loss of metal on the external and internal surfaces of the tubes, and finally structural failure (pinholes and cracking) of the weakened and thinned tubes.

Deterioration of external walls is, in general, caused by carburization, which has two effects: (1) it reduces the surface ductility of the tube virtually to zero so that thermal and/or biaxial stresses can cause surface cracking, and (2) it causes formation of a low-melting carbide, which is very fluid and is readily blown away, causing metal thinning.

Inside the tubes, the Aerozine-50 (50/50 hydrazine/unsymmetrical dimethyl hydrazine) decomposes and the tubes become internally carburized and nitrided; the surface ductility becomes low and cracks are formed. Some metal loss occurs, probably through dislodging of the very brittle carburized-nitrided layer by nitrogen gas.

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13. ABSTRACT

In designing regeneratively cooled thrust chambers, the heat transfer conditions are selected to avoid "burnout" situations. Failure in engines using storable propellants during development, test, or operation seldom occurs by the burn-out mechanism of design.
Roughening, pinholing, tube cracking, or splitting are common occurences because of metal disintegration either on the combustion chamber side or internally within the tube due to two processes: (1) the combustion gases from nitrogen tetroxide and Aerozine-50 reacting with the stainless tubing (Type 347), and (2) the decomposition products of the Aerozine-50 degrading the interior of the tubes. A mechanism of tube deterioration is developed to give a chronology of the events occurring from initial tube carburization to final tube failure.

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