# Deterioration of Stainless Steel Regeneratively Cooled Thrust Chambers

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**Although brazed tube, regeneratively cooled thrust chambers, operating on storable propellants {Nitrogen tetroxide, $N_2O_4$, and Aerozine-50 (50% hydrazine, $N_2H_4$, and 50% unsymmetrical dimethyl hydrazine, $N_2H_2[CH_3]_2$)} are designed by heat-transfer calculations to fail by burn-out conditions, failure is seldom by this mechanism. Failure is primarily related to carburization of the type 347 stainless tubing caused by the decomposition of the fuel component, unsymmetrical dimethyl hydrazine. The roughening, pinholing, cracking, and wall thinning are related to the carburization and, to a lesser degree, nitriding. Deterioration occurs both internally, from the decomposition of the coolant (fuel), and externally, from the combustion of the propellants, particularly in regions of film cooling.**

## Introduction

REGENERATIVELY cooled thrust chambers used for booster applications are often made from thin-wall tubing of type 347 (18Cr 8Ni + Cb) stainless steel. These tubes are about a half-inch in diameter with walls 12 to 16 mils thick 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. Engines are designed to operate at around 760°C (1400°F) metal temperature in the throat area, which is the hottest zone of the operating engine.

In the application discussed here, the engine operates on storable propellants, nitrogen tetroxide as the oxidizer and Aerozine-50 as the fuel. The engine is designed on the basis of a burn-out criterion—a condition where the excessive heat flux in the chamber cannot be accommodated by fuel flow in the tubes. In such case, the tube temperatures rise, and the tubes rupture from lack of high-temperature strength. However, failure is seldom by this mechanism. This paper will show that the primary cause of failures (observed as tube cracking, wall thinning, or pinholing) is metal disintegration either on the combustion chamber side or internally within the tube. It has been shown that metal disintegration is caused primarily by external carburization and internal carburization and nitriding. The metal-gas reactions involved lead to some unique metal failures.

Carburization is the metallurgical phenomenon by which carbon is introduced into the surface of a ferrous material by the diffusion process. The source of carbon can be a carbonaceous gaseous medium or a liquid such as molten cyanide. Nitriding is a similar phenomenon except, of course, that nitrogen is the diffusion specie; hydrazine is an excellent nitriding medium. Consequences that occur as a result of carburization are as follows: the steel loses its stainless quality (aqueous corrosion and oxidation resistance are impaired), the mechanical properties are harmed, there is often the loss of metal from either surface of the steel, the tubes crack, and pinholes are formed in them.

Stanley[1] has shown that carburization of type 347 austenitic stainless steels occurs in one hour at 800°C (1470°F) and becomes progressively rapid so that significant carburization can occur in one minute at 1000°C (1832°F). Schley and Bennett[2] showed that cast furnace tubes (30Cr, 20Ni, bal. Fe) can fail in service at 1100°C (2210°F) as a result of high nitrogen content. Porosity and blisters can develop in presence of carburization and overheating. These authors point out that the carburized steel melts about 1288°C (2350°F), whereas the HL alloy 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 release of gaseous nitrogen. These observations will be pertinent in the discussion.

The failure of regeneratively cooled rocket booster engines in development and testing prompted the present study to explain reasons for the deterioration of thin-wall tubes of AISI type 347 stainless steel used in their construction.

## Materials and Procedures

The initial industry selection of type 347 for thrust chambers was largely predicated on the use of type 347 (columbium-stabilized) over type 321 (titanium-stabilized) because cleaner braze joints are produced. The stabilized grades were preferred over types 304 and 316 because of corrosion considerations. Table 1 shows the nominal chemical analyses of these grades.

A section of brazed tubes from a chamber is shown in Fig. 1 to illustrate the type of structure that is produced. Heat marking occurs near the bifurcated joint. Terminal blocks were installed for flow measurements. Over-all length is about five feet. In chambers made with single tubes, heat marking also occurs. Gold-base and manganese-base brazing alloys are used for joining these stainless tubes into an integral, gas-tight chamber.

A metallographic study was first carried out on some type 347 tubes that were experimentally failed under burn-out, i.e., high heat flux conditions.† Such information was desired to establish the nature of tube failures resulting from burn-out conditions around which an engineer designs a rocket engine.

Subsequently, metallographic studies were initiated to understand the nature of pinholes, cracks, roughening, and tube splits on development and production hardware. Microprobe analyses were also conducted for carbon and nitrogen.

Guided by the metallographic structures found in failed tubes on thrust chambers, experiments on carburization and

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† These samples were furnished by A. C. Kobayaski of Aerojet-General Corp., Sacramento, Calif.

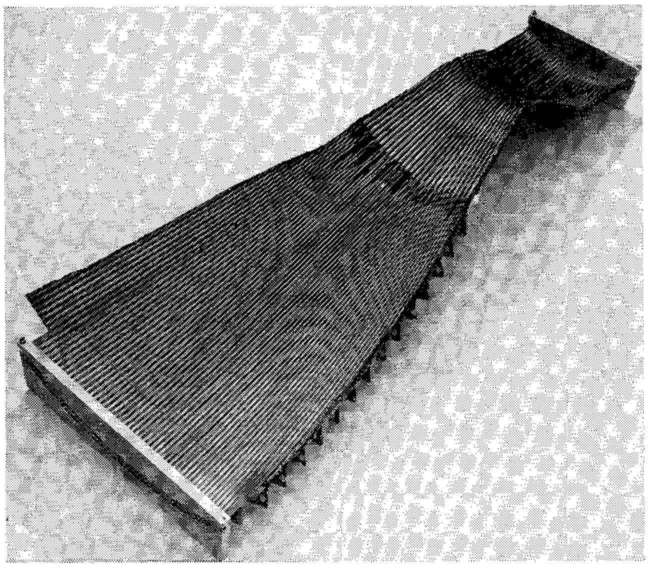

**Fig. 1 Rocket engine section showing brazed tube construction and heat marking.**

nitriding were performed in order 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 were also nitrided in ammonia and tensile tests were run.

## Results

### Examination of Burn-Out Samples

Burn-out tests were run using electrically heated tube sections fabricated from type 347 stainless steel. In the burn-out tests, the test section was protected by a nitrogen atmosphere while Aerozine-50 circulated through the tube. The heat flux was increased stepwise until burn-out failure of the tube occurred.

Figure 2 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 tube and carbonaceous deposit in the region of failure Flaring is caused by the biaxial stresses resulting from the internal pressure in the tube at the moment of rupture. The carbonaceous deposit results from the decomposition of the UDMH in the Aerozine-50.

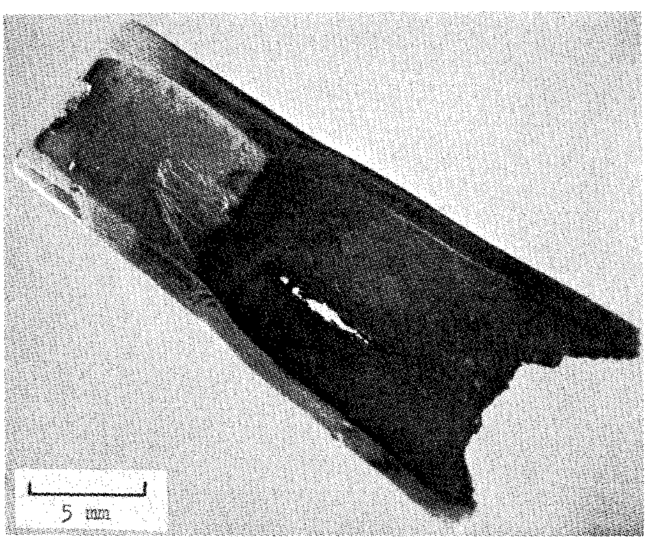


**Fig. 2 Failure of type 347 tubing under burn-out conditions.**

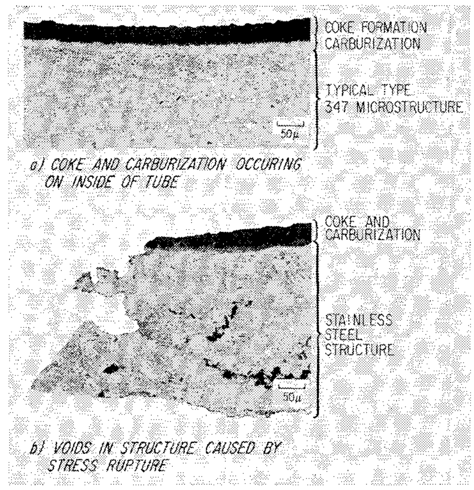


**Fig. 3 Edge of fracture on burn-out failure.**

Photomicrograph Fig. 3a shows the coke formation and some carburization beneath the coking on the inside of the tube in the vicinity of the failure (burn-out). Figure 3b shows the edge of the fracture and the voids show the metal was separating at the elevated temperature.

### Nature of Deterioration

Five types of deterioration have been observed on the brazed tube bundle on the chamber side of production engines: a) heat-marking of certain tubes in chamber, b) beads or crystallized material, c) roughening, d) pinholing, and e) tube cracking.

Heat-marking is defined as the discoloration of the type 347 stainless steel tubing that occurs in the thrust chamber and is usually located below the throat. In regeneratively cooled thrust chambers, only isolated tubes, generally up-tubes, will show heat-marking whereas 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 carburization is only brought out by etching. Chemical analysis, of course, confirms the presence of carbon. Figure 4 shows the appearance of a section of a heat-marked tube. Note that on either side, the tubes are bright except for the splatter of braze metal removed from between the tubes. A heat-marked tube is a carburized tube. See Fig. 5, which shows a photomicrograph of such tube. The tube surface shows a thin layer of a carburized structure. The grain size is also coarse (ASTM grain size is 5.5, compared to an as-received ASTM grain size of about 10).

Because carburization of type 347 stainless steel only occurs above about 780°C (1530°F), the tubes must have experienced rather high temperatures.[1] Tube temperatures above 780°C are not unreasonable in the engines. The coarse grain size in Fig. 5 suggests temperatures as high as 1095°C (2000°F).[3]

Occasionally, there is observed on the combustion side of the chamber solidified beads or crystallized material that had

**Table 1 Nominal compositions of stainless steels**

| AISI type | Composition, % Cr | Ni | Cb | Ti | Mo |
|---|---|---|---|---|---|
| 304 | 19 | 10 | ... | ... | ... |
| 316 | 17 | 12 | ... | ... | 2.5 |
| 321 | 18 | 10 | ... | 0.5 (approx) | ... |
| 347 | 18 | 10 | 0.8 (approx) | ... | ... |


**Fig. 4 Heat-marked (black) tube in vicinity of bright tubes.**

apparently melted from the tubes. Figure 6a shows a beaded spray and Fig. 6b shows the crystallized material. This material had been assumed to be molten metal, but x-ray analysis identified it as carbide, $Fe \cdot Cr_7C_3$, that had formed, melted, and resolidified.

Various melting temperatures have been observed for this carbide, some as low as 1095°C (2000°F) and some as high as 1260°C (2300°F). Variation in melting temperature is probably due to different carbon contents in the carbide.

Roughening of tube material is often observed. Roughening due to the resolidification of remelted braze material has been referred to before (see Fig. 4). Carbide deposits are shown in Fig. 6. Roughening, representing metal loss, is often found in association with pinholes and cracks.

Pinholes, such as shown in Fig. 7, are perforations of the tube wall. The holes are always in a roughened area, often in association with cracks.

The carburizing atmosphere causing carbon pickup comes mainly from film cooling by the fuel, i.e., Aerozine-50. Obviously some of the up-tubes run hotter than others because of differences in heat transfer to the circulating fuel inside. The reason for these differences is obscure.

Tube cracking, sometimes transverse and sometimes longitudinal, is often observed on overheated tubes. These types of cracking are shown in Fig. 8. Longitudinal cracks, when they penetrate the wall, are called splits.

## Discussion of Failure Phenomena

### Burn-Out

In the advanced heat-transfer situation, when the coolant (fuel) in the tubes can no longer carry the imposed heat flux, the temperature of the tube rises. Nucleate boiling occurs and later film boiling. (For a discussion of these phenomena, see Refs. 4 and 5.) In later stages of film boiling, the metal temperature rises rapidly and can approach the melting point. Before the melting point is reached, the metal strength is decreased to such extent that the hydrostatic pressure of the coolant deforms, and often ruptures, the tube.

It may be stated here that none of the failed engines showed this type of structure—which may be referred to as classical burn-out.

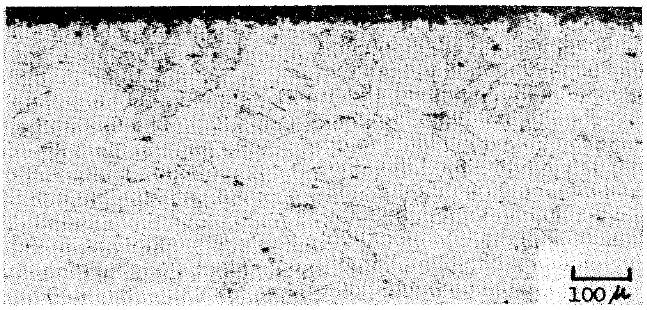


**Fig. 5 Microstructure of heat-marked tube shows carburized (mottled) layer and coarse grain size.**

### 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) and chamber. The film cooling tends to make the combustion products in the chamber carburizing to the tubes. Nitriding was expected but not found. Virtually no oxidation occurs unless there are wide variations in the mixture ratio or film cooling is insufficient.

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

Sections through pinholes and cracks showed carburization on the outside of the stainless tubes and carburization and nitriding on the inside, although sometimes only carburization is observed on the inside. In addition to the carburization and nitriding, there is evidence of metal loss on both sides that

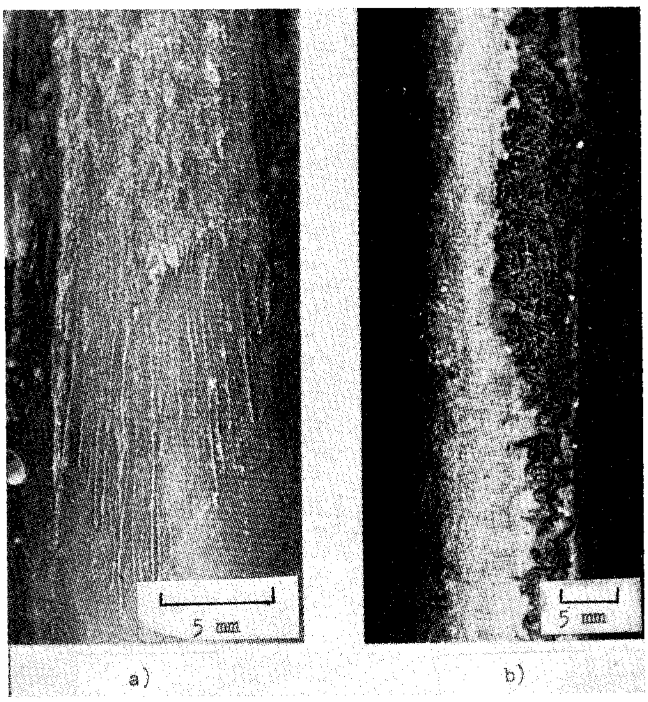


**Fig. 6 Two types of resolidified carbide, $Fe \cdot Cr_7C_3$: Beaded spray and crystallized.**

‡ For the engines studied, the chamber pressure was in excess of 800 psia and temperature in excess of 5500°F. Combustion products contain both carburizing and nitriding constituents. A typical analysis would contain: CO—0.9 to 3.3%; $C_2H_5$—0.4 to 1.3%; $N_2$—16 to 35%; $NH_3$—15 to 60%; $CH_4$—6 to 17%; $H_2$—13 to 37%; HCN—0.1 to 2.8%; $C_2H_4$—0.2 to 0.8%; and $CO_2$—0.1 to 0.8%.

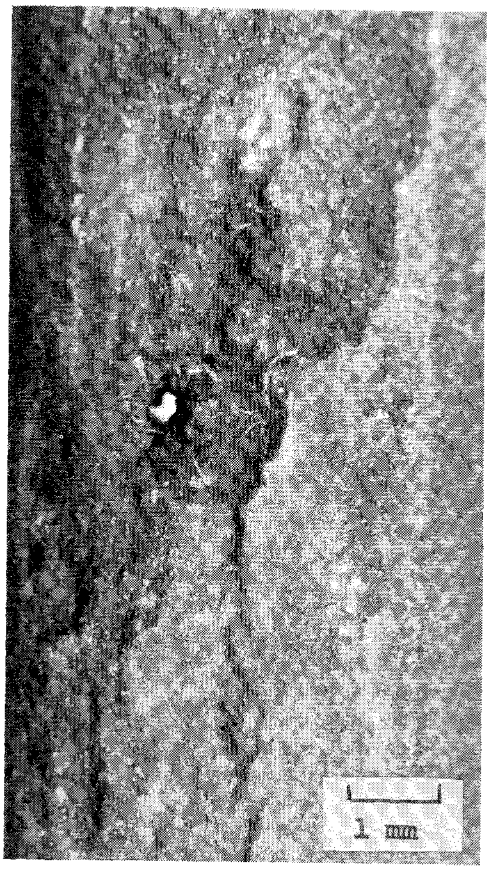


**Fig. 7 Pinholing and associated roughening.**

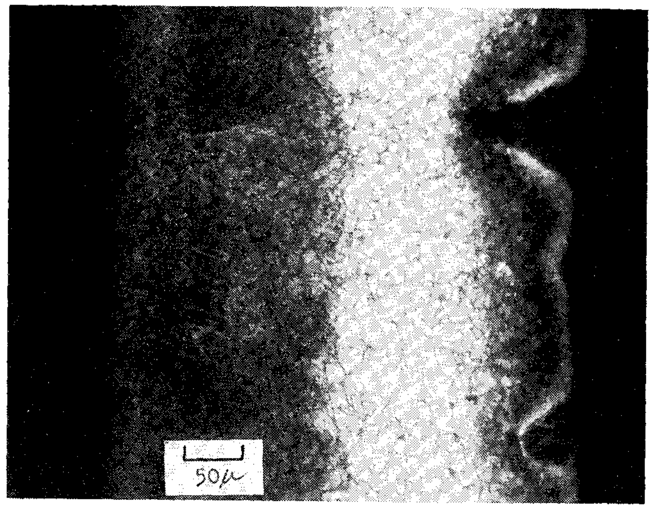


**Fig. 9 Microstructure of distressed type 347 stainless steel tube.**

causes a thinning of the wall. Metal loss mechanisms on either side are probably of different types. Obviously, as wall thinning proceeds, tube failures characterized by roughness, perforations, cracks, and splits are likely to occur.

Figure 9 shows the microstructure in the vicinity of cracks. Note carburization (black areas) on the external surface. Note the carburized (black) and the nitrided (white) zones on the internal surface. Severe metal loss on the internal diameter and crown cracking are shown in Fig. 10. Carburization on the crown is absent, but it may have melted away. The internal surface shows a porous structure of carbide and nitride that apparently is readily detached.

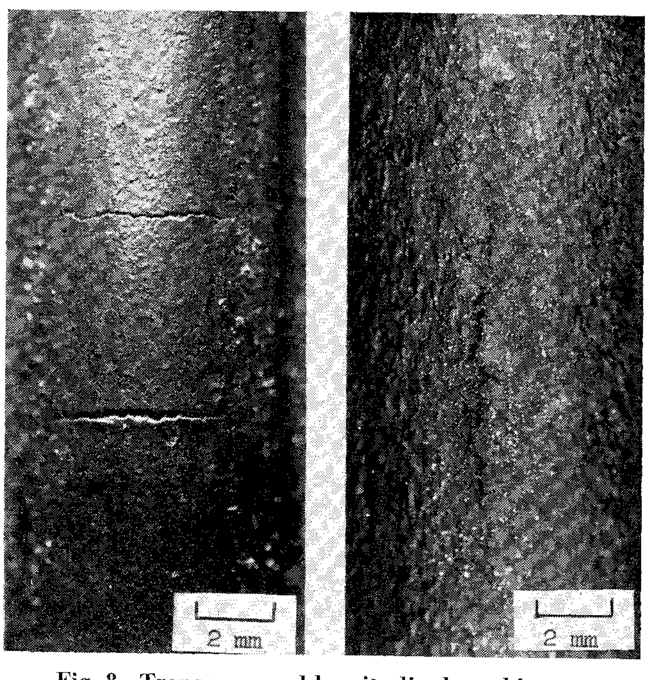


**Fig. 8 Transverse and longitudinal cracking on distressed tubes.**

One unfortunate consequence of the carburization is the loss of ductility of the carburized type 347.[6] Figure 11 shows the loss of ductility (i.e., elongation) of the steel with carburization. Figure 8 shows the type of transverse cracking that also develops when a carburized steel is pulled in tension. The formation of a nitride case lowers the ductility of the type 347 even more than does the carburization,[7] and similar cracking also occurs.

During firing and refiring, the chamber obviously experiences considerable dimensional change, and superimposed on these changes is the stress from the biaxial stresses from the hydrostatic pressure of the coolant. Hence, if the carburized and/or nitrided steel has limited ductility, cracks will develop. Whether the cracks are transverse or longitudinal depends on what type of stress predominates.

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

### Internal Carburization and Nitriding

Microprobe traverses were made on the internal surface to identify the carbide and nitride zones (see Fig. 12). The traverse verifies the observation made in Fig. 9 that the nitrogen is on the immediate surface. The dark-etching zone is a carburized structure consisting of carbide ($Fe\cdot Cr_7C_3$) and austenite (face-centered cubic solid solution). The light etching constituent on the inside surface of the tube, superimposed on the carburized layer, is a nitride ($(Fe\cdot Cr)N$).

Obviously, the carbide, because of its extensiveness, and probably to some extent the nitride, cause a reduction in ductility, and with dimensional changes resulting from thermal transients, cracks develop. However, in addition to the notches (cracks), there appear to be large areas internally where metal has been dislodged from the distressed areas (Fig. 10).

With the type of 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, there is no evidence of classical burn-out where the heat flux is so high that the temperatures of the tubes rise and the tubes merely rupture because of the biaxial stresses in the tube.

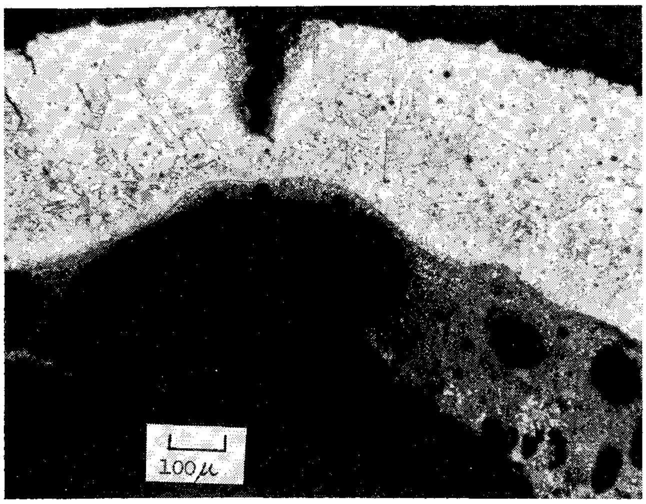


**Fig. 10 Microstructure of another distressed area showing cracking and wall thinning.**

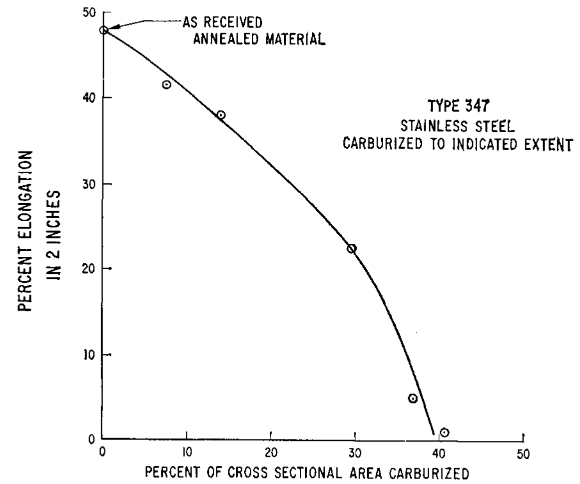


**Fig. 11 Curve shows a decrease in ductility (elongation) when the stainless steel becomes carburized.**

Some details of the total picture of tube deterioration 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 coolant fuel (Aerozine-50) in an operating engine sometimes unpredictably experiences a diminution of flow rate in certain up-tubes. With a lowering of flow in some of the tubes, the tubes start to run hot. The first visible signs of hot spots are the observance of heat marked, discolored, i.e., carburized, areas. This effect is strangely localized; adjacent tubes may remain unaffected, i.e., bright.

Because heat marking occurs at or above about 780°C (1530°F), the tube is obviously operating above its design temperature. Examination of the tube wall on the opposite (inside wall) shows that sooting has taken place. The implications of these sooty deposits is that film boiling has occurred and the coolant has decomposed. The rising temperatures caused 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:

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

or

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

Thereafter, the hydrazine fraction decomposes:

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

$$NH_3 \rightarrow N_2 + 3H_2$$

Once decomposition starts, both carbon and nitrogen are available for diffusion into the steel.

Nitrogen from any of these reactions causes nitriding. Because nitriding is also a slower diffusion process than carburization in this steel, the nitrogen concentrates mainly at the inside surface.

Because of film boiling, the tube cannot remove heat rapidly enough and the temperature continues to rise. Hence, damage to the tubes occurs, especially above 780°C (1530°F). Simultaneously, thermal stresses and biaxial stresses are operating. Because carburized tubes have limited ductility, they crack externally and internally as the photomicrographs show. Cracked surfaces also carburize, further weakening the structure.

As the temperature rises, the surface carbide melts and is blown away. Removal of the molten carbide results in surface roughening and wall thinning and the tube wall is less able to withstand the combined stresses. Some carbon, of course, continues to diffuse into the steel. Conceivably, existing cracks can propagate more easily under these conditions.

Internally, carburization and nitriding begin simultaneously. As carbon and nitrogen diffuse, they cause embrittlement.

There is another unfortunate consequence of this carburization and nitriding inside the tube. When the chromium content of this steel has been depleted by the carburization and nitriding processes, the alloy becomes susceptible to blister and void formation. The removal of chromium from the austenite by carbon favors the release of gaseous nitrogen from the low chromium austenite.[2] Release of nitrogen gas could well displace the brittle carbide and nitride layers. The removal of the porous carburized and/or nitrided internal layers would also be a metal removal (wall thinning) process.

Eventually, a puncture or pinhole occurs in a cracked area or where the metal has been severely thinned from both sides. This thinning is not always a uniform process. In regions where thinning tends to be of greater extent, vertical rupture cracks are observed.

No attempt has been 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. For aero-

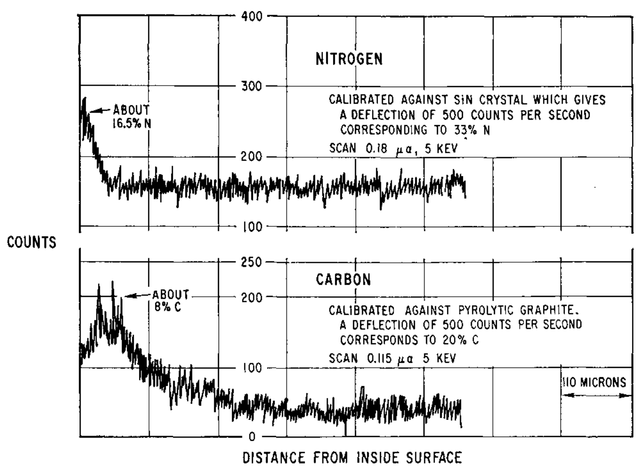


**Fig. 12 Microprobe traverses on the inside of a distressed type 347 stainless steel tube.**

space applications, stainless steels higher in alloy than type 347 have not been used. Where higher strengths at elevated temperature are required, superalloys have been used, e.g., Inconel-N on the F-1 engine.

## Conclusions

Brazed tube, regeneratively-cooled thrust chambers employing storable liquids (nitrogen tetroxide and Aerozine-50), seldom fail under classical burn-out conditions. Failure mechanisms observed are related to the actual deterioration of stainless steel tubing. Gas-metal reactions (i.e., carburization externally, and carburization and nitriding internally) occur that result in loss of ductility, metal loss on the exterior and interior of the tubes, and, finally, in structural failure (pinholes and cracking) of the weakened and thinned tube.

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# Control Jet Interaction Investigation

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**An investigation of the interaction of control jets with the airstream surrounding a typical tactical missile configuration is reported. Rear-mounted bistable fluidic thrusters and circular sonic jets using air, nitrogen, and helium produced jet force amplification factors of about 1.6 to 2.2 at Mach numbers 0.9 to 2.0. Amplification factors near unity were measured at Mach 0.6. In general, amplification factors for a finned configuration were higher than for the model without fins.**

## Nomenclature

$a_\infty$ = freestream speed of sound
$A_J$ = jet throat area
$C_N, \Delta C_N$ = normal force coefficient and increment from interaction
$C_{N\alpha 0}$ = normal force coefficient slope $(dC_N/d\alpha)$ at $\alpha = 0$
$D$ = reference length (body diameter)
$f$ = fluid jet switching frequency
$F_I, F_J$ = interaction and jet forces
$K$ = jet interaction force amplification factor
$M_J, M_\infty$ = jet exit and freestream Mach numbers
$\dot{m}_P$ = jet mass flow rate
$P_e, P_J$ = jet exit and jet chamber pressures
$P_\infty$ = freestream static pressure
$q_J, q_\infty$ = jet exit and freestream dynamic pressures
$V_{exit}$ = jet exit velocity
$X_{cp}$ = center of pressure
$S$ = reference area (body cross section)
$\alpha$ = angle of attack
$\gamma$ = ratio of specific heats

## Introduction

The interaction between a control jet and the moving external airstream surrounding a missile can, under certain conditions, amplify the force of the control jet alone by a jet interaction (or amplification) factor $K$. Although numerous investigators have discussed jet interaction theory and test data at supersonic or hypersonic freestream conditions,[1–4] only limited data are available for subsonic or transonic conditions. Reference 5 discusses effects of jet gas molecular weight and jet exit Mach number $M_J$ on amplification factor and jet penetration and correlates test data with Dahm's[6] theoretical prediction. Cassel[7] reports amplification factors of 0.5 to 0.9 for forward located jets at subsonic conditions. Kuiper[8] presents data for steady-state jets similar in shape to those reported herein which show the same amplification trends. However, his values of $K$ never go below 1 subsonically and peak near 2 at $M_\infty = 1.0$, whereas the present data peak at about $K = 2.3$ near $M_\infty = 1.2$.

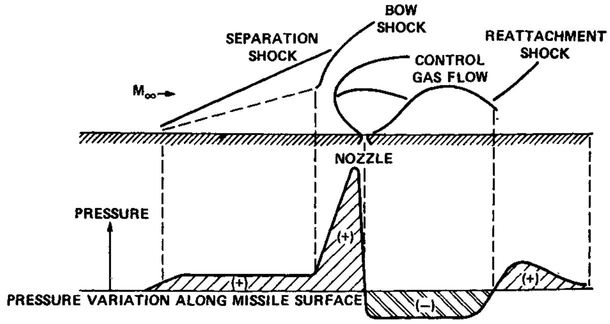


Fig. 1 Jet interaction phenomenon.

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