Failure Mechanisms in Dense Tungsten Alloy Rocket Nozzles

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In the study of dense tungsten alloys for uncooled nozzle service, two principal failure mechanisms were found: erosion by chemical reaction with the propellant combustion gases and cracking due to thermal stress. In laboratory tests of heated filaments, the major chemical attack was oxidation by CO_2 and H_2O; the presence of CO and H_2 markedly reduced these oxidation reactions. These conclusions on the reaction mechanism were substantiated by the erosion observed in subscale motor firings. Thermal-stress cracking was also studied in motor firings; it occurred early in the test from tensile stresses at the outer surface. Thermal upsetting from compressive stresses at the inner surface was noted. The fracture resistance of cast tungsten was superior to powder-process tungsten, and "hot working" generally increased the tendency to crack. Large grain size was superior to small grain size.

Introduction

THE use of an uncooled nozzle is desirable to maintain the inherent simplicity of a solid-propellant rocket motor. The severe environmental conditions produced by high-performance, metalized, solid propellants have presented a very real challenge in the search for good nozzle materials. With propellant flame temperatures generally above 6000°F and often as high as 6500–6600°F, tungsten and high tungsten alloys stand today as the prime candidates for uncooled nozzles. Just a few years ago when tungsten was used for hardware items, only a powder metallurgy product was available. Significant progress has been achieved with sintered tungsten, especially in combination with infiltrants in the porous matrix, but room for improvement is apparent. More recently, dense-cast tungsten, which offers possibilities of improved performance, has become available for nozzle hardware.

In the present study of dense tungsten, two principal failure mechanisms were found. One involves erosion by chemical reaction between propellant combustion gases and tungsten. The other is thermal-stress cracking, which leads to nozzle assembly destruction. The chemical composition of the propellant combustion products varies widely for various propellant formulations. The most significant components involved in reactions with tungsten alloys are the oxidizing species CO_2 and H_2O and their products of oxidation CO and H_2. A convenient method of correlating the roles of these species is in terms of the ratios CO/CO_2 and H_2/H_2O. In addition, HCl (commonly produced from perchlorate oxidizers) and HF (from fluorine-containing propellant ingredients) might be expected to react with tungsten nozzles. Table 1 lists these important chemical parameters for several generic classes of solid propellants. The results of laboratory studies presented in this paper show the importance of these parameters.

Laboratory Study of Chemical Reactions

Two techniques were used to elucidate the nature and extent of the chemical interaction between tungsten alloys and combustion products. In the first method, the effects of single constituents and of simple gas mixtures were studied by heating wire specimens in selected atmospheres. In the second, wires were exposed directly to the complex combustion environment in the flame of a propellant strand burned in a pressurized optical bomb.

Heated Wire Tests

The heated wire tests were made in a glass vacuum system shown in Fig. 1. A filament of the tungsten wire to be tested (25-mil diam, $2\frac{1}{2}$ in. long) was weighed and mounted in the vacuum flask. After the filament was in place, the flask was purged, evacuated, and filled to the selected pressure with the reaction gas. The filament was heated by passing an electric current through the wire. A water-cooled cold finger directly above the filament served to collect products that vaporized from the refractory wire. The principal data collected in each test were the filament temperature, the weight change of the filament, the time to filament burnout if burnout occurred, and visual observations of the effect of the gas on the wire. If volatile products were formed, these were noted. If sufficient deposits were formed on the cold finger, they were recovered for further analysis.

Tungsten reacted rapidly with carbon dioxide, and sustained substantial weight loss. A heavy oxide deposit, ranging in color from pale green to dark blue, appeared on the cold finger. No reaction layer could be found on the filament after burnout, because the oxides formed had evaporated. A few small, scattered areas of surface penetration by the oxide were observed metallographically. The reactions with water vapor were similar to those with CO_2, except that they oc-

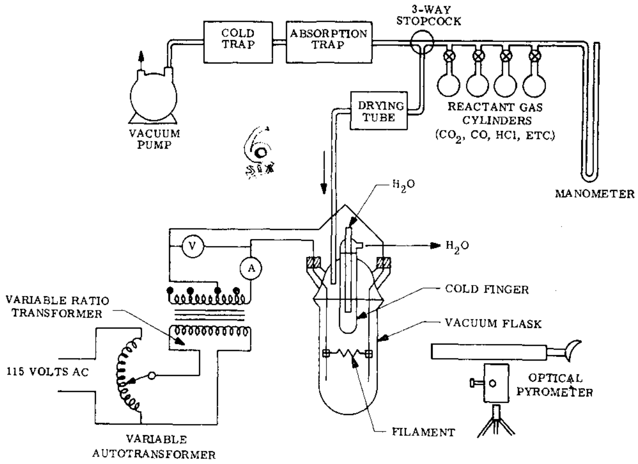

Fig. 1 Filament test equipment.

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Table 1 Typical chemical composition products for solid propellant

Propellant type	Total, $CO_2 + H_2O$, percent	Mixture ratios CO/CO_2	Mixture ratios H_2/H_2O	HCl content, percent	HF content, percent
Simple composite	up to 50	1	0.1–0.2	20–25	...
Aluminized composites					
Balanced formulation	5	70	9	10–15	...
Oxidizer-rich formulation	10–15	20–30	3–4	10–15	...
Fluorine-containing formulation	up to 10	5–20	1–3	variable	20

curred more rapidly. The color of the condensed tungsten oxide from the filament varied from greenish yellow to blue to black as the oxidizing gas pressure was reduced. X-ray diffraction analysis suggested that all the oxides were of the WO_3 type, which become oxygen-deficient as the blue color predominates (probably $W_{20}O_{58}$).

Reactions with HCl were less destructive than those with CO_2. A small weight loss occurred, but the appearance of the filament was not altered. Microscopic examination showed no reaction layer. Tungsten was affected only slightly by HF and showed no reaction with CO.

The principal reactions noted were the oxidation reactions

$$W\ (c) + 3\ CO_2\ (g) = WO_3\ (g) + 3\ CO\ (g) \quad (1)$$

$$W\ (c) + 3\ H_2O\ (g) = WO_3\ (g) + 3\ H_2\ (g) \quad (2)$$

The presence of substantial concentrations of CO and H_2 would be expected to reduce the oxidation rates, at least in proportion to the approach to equilibrium composition, and temperature would be expected to have a significant effect. To check these hypotheses, tests were carried out in selected gas mixtures. Since completely volatile oxidation products are formed, weight losses are a direct measure of the extent of reaction.

Data were taken in a series of one-minute exposure tests at temperatures of 3600°, 4000°, 4400°, 4800°, and 5200°F. At each temperature, the weight loss was measured after exposure to various CO/CO_2 and H_2/H_2O mixtures. For the CO-CO_2 system, mixture ratios from 0 to 62 were used, and for the H_2-H_2O system, ratios from 0 to 9.7 were used. In both systems, the low ratios are characteristic of the combustion gases from

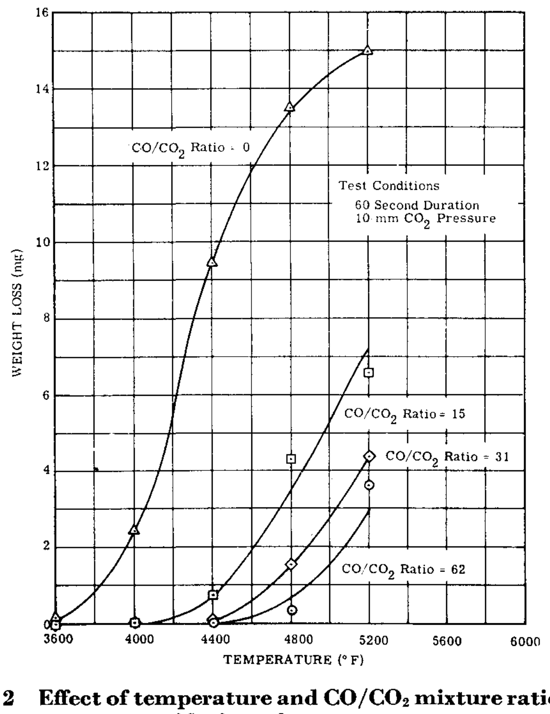

Fig. 2 Effect of temperature and CO/CO_2 mixture ratio on oxidation of tungsten.

nonmetalized solid propellants and many liquid propellants at balanced oxidizer/fuel ratios. The highest ratios represent the composition from a balanced, aluminized propellant formulation. The intermediate ratios are typical of the combustion products from oxidizer-rich aluminized propellants commonly formulated to achieve maximum combustion efficiency.

Figure 2 shows the oxidation losses are greatly reduced as CO/CO_2 ratio is increased: with $CO/CO_2 = 30$, a temperature approximately 900°F higher is required to achieve weight losses equivalent to those found in pure CO_2. Figure 3 similarly shows data obtained in H_2/H_2O mixtures at various temperatures. Again, the decreased oxidation as the temperature decreases (or the H_2/H_2O ratio increases) is clearly evident.

Propellant Strand Tests

The second phase of the laboratory study involved the direct exposure of wires to burning strands of solid propellant. In a typical test, a tungsten wire, usually 25 mils in diameter, was embedded in a strand of the selected propellant, approximately $\frac{1}{4}$ in. square and 6 in. long, by curing the propellant around the wire. In other tests, the wire was held above the propellant to vary the severity of the exposure. The propellant and wire were installed in an optical bomb (Fig. 4) provided with two windows for high-speed motion pictures. The bomb was pressurized with nitrogen, and the propellant was ignited at its upper end; burning times varied from 1 to 6 sec, depending on the type of propellant and the pressure. The wire residue was then recovered for examination. Examination of the wire included weight changes, visual observation, metallographic examination, microhardness measurements, and x-ray diffraction analysis.

Tungsten wires exposed to the flame of an oxidizing, nonaluminized composite propellant lost considerable weight, but no surface reaction layer remained that could be identified by microscopic or x-ray diffraction analysis. The losses clearly occurred by oxidation to a volatile product. When exposed to a balanced, aluminized propellant flame, tungsten showed a carbide reaction layer as illustrated in Fig. 5. X-ray diffraction established the presence of αW_2C. An eutectic-type structure W-W_2C had probably formed. The high microhardness of the carbide area (1125 KN) further indicates the presence of the carbide. Deposits of αAl_2O_3 and the oxycarbide $Al_2O_3 \cdot Al_4C_3$ were identified by x-ray diffraction. At higher burning pressures, the reaction layer was considerably thinner.

Tungsten wires exposed to a fluorine-containing propellant showed small weight increases and were covered with gray-yellow beads. The amount of deposit diminished and the color faded at higher burning pressures. Most of the wire length was recovered. Metallographic examination of these wires showed that tungsten was virtually unaffected and showed no reaction layer.

Comparison of Laboratory Data with Nozzle Performance

The laboratory data cannot be compared directly to motor test results since these laboratory tests do not reproduce all of the conditions in a rocket nozzle. Nevertheless, filament

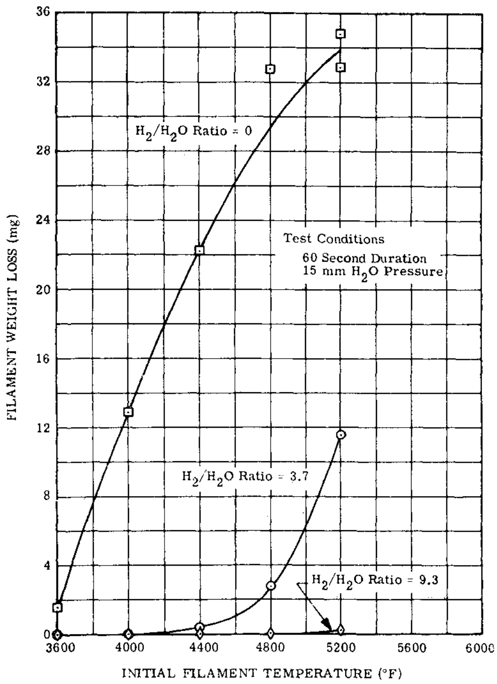

Fig. 3. Effect of temperature and H_2/H_2O mixture ratio on oxidation of tungsten.

tests and propellant strand tests demonstrated conclusively that CO_2 and H_2O are the gas constituents most reactive with tungsten, and motor-nozzle tests are in agreement in every case. An oxidizing, aluminum-free propellant causes more erosion, for example, than an aluminized propellant, because of the CO_2 and H_2O formed by the aluminum-free propellant. Little effect was noted on tungsten exposed to burning strands of an aluminum-containing propellant except for a tendency for carbides to form and melt. In motor nozzle tests, tungsten is essentially unaffected except in severe tests in which some slight deterioration occurs in the nozzle approach section. Carbides have been observed in this area.

In propellants containing a perchlorate oxidizer or a polyvinyl chloride binder, HCl is produced as a combustion product. The lack of significant reaction between tungsten and HCl in the filament test is in agreement with rocket motor experience that tungsten nozzles serve equally well with chlorine-containing and chlorine-free propellant.

Only slight reaction was observed (up to 5500°F) between HF and tungsten; thus, tungsten should be serviceable as a nozzle for motors with fluorine-containing propellants of moderate flame temperature if other reactive constituents are not present in large quantities. The effects of HF on tungsten at higher temperatures were not investigated.

Effects of Alloy Addition on Chemical Reactions

The addition of 3% rhenium was found to reduce the oxidation rate of tungsten moderately. A slight, further reduction was noted at 25% rhenium content. Thoriated tungsten (2% thoria) appeared slightly more resistant than pure tungsten to oxidation by H_2O, but no difference was found in oxidation by CO_2.

It should be realized that the presence of alloy ingredients may modify the thermal stress fracture resistance of tungsten as well as affect the chemical reactions. Thus, as long as alloy additions do not seriously degrade the chemical behavior of tungsten, they should be explored as agents to improve ductility or strength and to decrease thermal cracking. This approach is currently being followed in motor firing nozzle tests similar to those described in the following sections on thermal stress fracture studies.

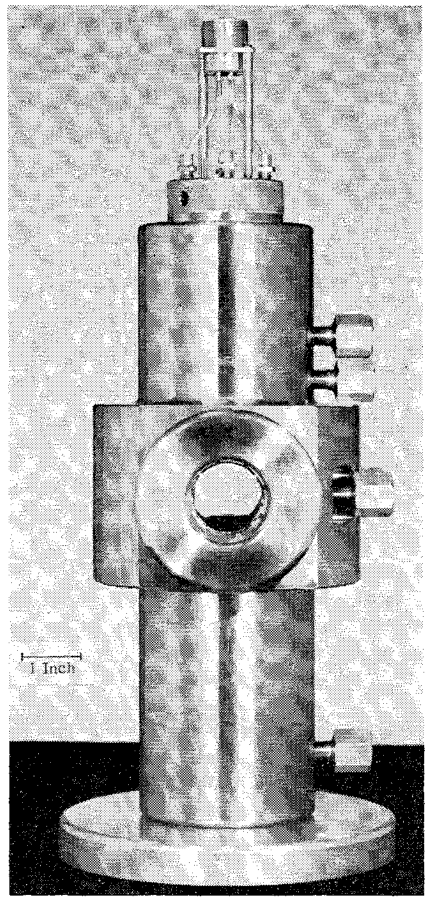

Fig. 4 Strand-burning optical bomb.

Chemical Reactions in Subscale Motor Nozzle Tests

As indicated previously, the erosion resistance of tungsten exposed to highly aluminized solid propellants is good. Careful examination of the pressure-time curves for firings with different propellants and different tungsten materials does indicate something of the nature of the propellant combustion gas action on tungsten, however. In Fig. 6 three selected pressure-time curves are shown. Firing B-90 was made with a pressed, sintered, and forged tungsten nozzle and a 6600°F, moderately over-oxidized propellant. Firings F-12 and F-15 utilized a 6540°F, highly over-oxidized propellant. The nozzle in F-12 was the same type of tungsten used in B-90, but the nozzle in F-15 was a thoriated-tungsten alloy.

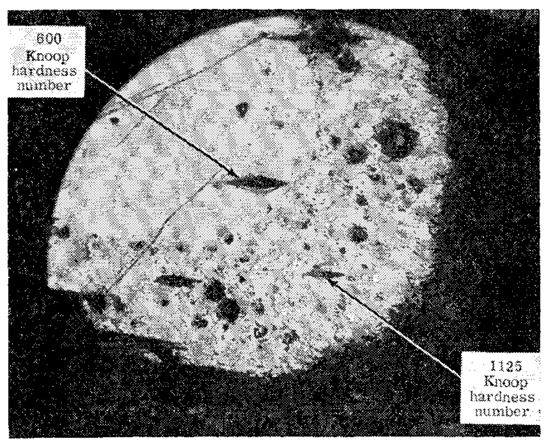

Fig. 5 Cross section (X300) of 0.025-in. tungsten wire exposed to aluminized propellant.

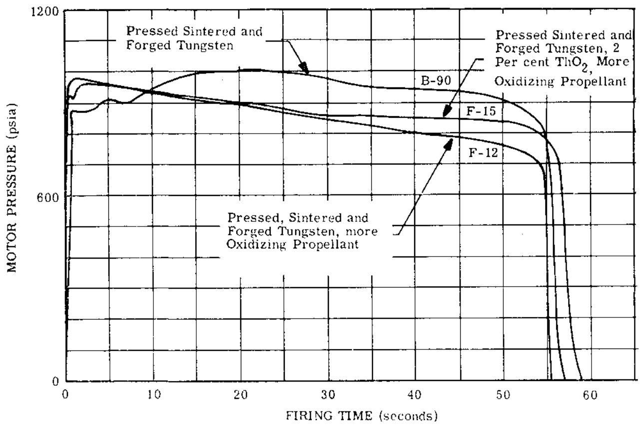

Fig. 6 Motor pressure traces for pressed, sintered, and forged tungsten.

The shape of the pressure-time curve in firing B-90 is typical of many found for tungsten inserts. The maximum pressure, which occurs between 10 and 20 sec after ignition, is indicative of thermal upsetting, which reduces the throat area. In the later stage of the firing, regression of the pressure curve indicates a slow erosion process that is believed to be caused by chemical oxidation of the tungsten. Comparison of the regressivity of the three curves indicates that erosion of tungsten was significantly greater in the more oxidizing propellant. The addition of 2% thoria, however, appears to have reduced erosion in the more oxidizing propellant to a rate comparable with that of pure tungsten in the less oxidizing propellant. Quantitative erosion rates can be estimated by making a correction for the thermal upsetting based on the interior ballistics of the motor and a thermal expansion correction on the final nozzle diameter. Although both of these corrections may be somewhat inexact, the erosion rates that are calculated are reasonable estimates as shown in Table 2. These data demonstrate the importance of the oxidation potential of the propellant to the erosion of tungsten and the possibility of providing moderate improvement by alloy additions.

Thermal Stress Fracture Studies

Brittle fracture of tungsten nozzle inserts has been a problem, and the cracking and ejection of portions of tungsten inserts has brought about a certain amount of reluctance on the part of rocket engine designers to use tungsten in nozzle construction. Ejection of cracked portions of tungsten generally occurs in the early part of a firing cycle, although in some cases the cracked portions are retained for varying periods of time by the back-up material and may be released near the end of a firing cycle. The source of much of the cracking of tungsten nozzles is the thermal stress created by the extreme thermal gradient during the first part of the firing cycle. Immediately upon ignition, the gas side of the tungsten is subjected to a very high heat flux while the back side of the tungsten insert is still cold. Thermal expansion of the inside portion of the tungsten creates tensile stresses in the colder outside portion. At temperatures below 400° to 900°F, depending on the processing details, tungsten is brittle. It is, therefore, not surprising that cracks initiate on the cold side

Table 2 Corrected erosion rates for tungsten nozzles

Nozzle material	Oxidation potential of propellant	Erosion rate, mil/sec
Tungsten	moderate	0.04
Tungsten	high	0.19
Thoriated tungsten	high	0.04

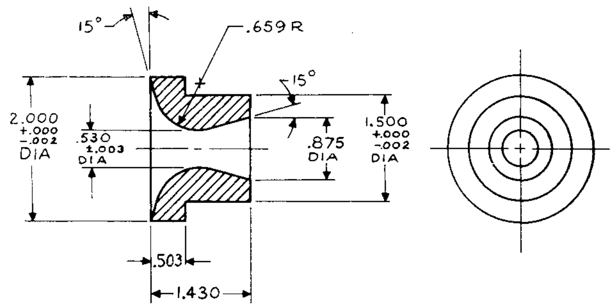

Fig. 7 Shoulder-retention-notched nozzle insert.

of the tungsten insert. The propagation of the crack is determined by many factors such as the stress level, the temperature of the uncracked portion, and the fracture toughness of the uncracked portion.

Motor Test Method

It is difficult to duplicate with laboratory equipment the thermal and stress conditions encountered in the nozzle of an actual rocket motor. The problem was, therefore, studied with subscale rocket nozzles tested in small rocket motors. The test piece was designed to be of sufficient thickness to introduce high thermal stresses, and the specimen was retained on a shoulder to induce typical retention stresses. The configuration of the nozzle test insert is shown in Fig. 7. Preliminary studies conducted with the Naval Research Laboratory indicated that a circumferential "*V*" notch, 0.040 in. in depth and with a maximum radius of 0.003 in., provided a suitable stress concentration for crack initiation. This notch is ground circumferentially on the outside diameter of the test piece opposite the throat section. This ground notch provides a uniform crack initiation source for each tungsten insert even though factors, such as surface finish and surface machining stresses, may vary on the other portions of the insert.

The circumferential notch ground on the outside of the test nozzle inserts is not characteristic of conventional rocket nozzle inserts. It was used in this series of tests to furnish a uniform crack nucleation source. The surface of actual rocket nozzles is usually finished with great care and with

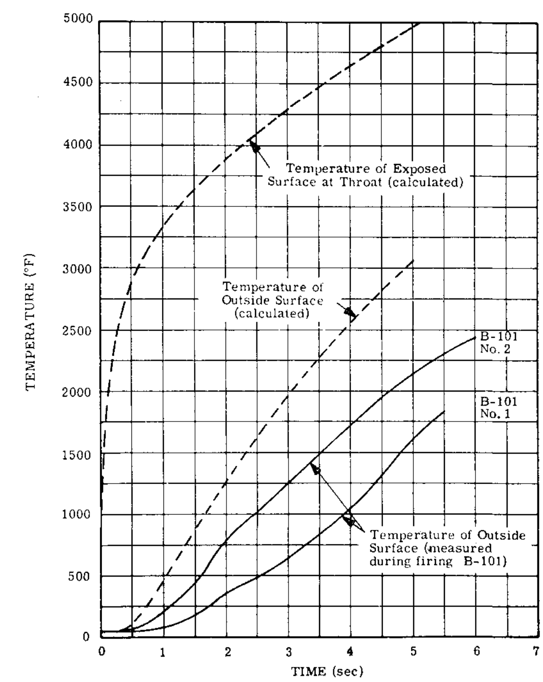

Fig. 8 Typical calculated and measured temperature-rise data for tungsten nozzle inserts.

special techniques to minimize stress concentrations. In spite of this procedure, cracks do occur in the nozzles of improved finish. Therefore, the comparison of materials on this basis is believed to be justified.

A high-energy propellant with a 6550°F flame temperature was used in the test firings. Limited tests with a 6000°F propellant indicated that the fracture tendency was substantially less with this relatively small decrease in flame temperature. The tungsten inserts were supported and insulated by a machined piece of baked carbon of low thermal conductivity. Typical temperature rise data measured on the back side of the dense tungsten inserts and calculated curves for the nozzle insert front and back surface temperatures are shown in Fig. 8. These data can be accurately calculated for the first few seconds of a firing by considering the tungsten as a heat sink with a minor correction for the effect of the rear wall interface with the insulating backup material. The rapid build-up of surface temperature produces large thermal gradients in the tungsten which cause high stresses and thermal cracking. Stress calculations for the nozzle configuration used in our tests lead to two major conclusions:

1) The gas-side temperature and compressive stress increase rapidly. Within a small fraction of a second, the stress will exceed the compressive strength, but the tungsten will generally be ductile and thermal upsetting can occur.

2) After approximately 1 sec, the tensile stress at the outside surface will approach 100,000 psi when the temperature is passing through the range of the tungsten ductile-to-brittle transition temperature. The exact relation between temperature, stress level, and transition temperature can be expected to influence the extent and nature of cold-side cracking.

As will be seen in the discussion of our experimental data, these analytical conclusions are in good agreement with the observed behavior of tungsten nozzle inserts. The stress analysis and the strain instrumentation that was applied in a number of firing tests were developed as part of a separate program conducted with the Naval Research Laboratory.[1]

Results of Thermal Stress Fracture Tests

Tungsten nozzles made by a variety of fabrication techniques, plus some nozzles made of tungsten alloys, were studied. The material types included pressed, sintered, and forged (to various degrees at various temperatures); arc-cast; arc-cast and extruded; arc-cast, extruded, and forged; fine-grain centrifugally cast; coarse-grain arc-cast; fine-grain cast material that was hot worked; and tungsten cast by the thermit process. Needless to say, because of the difficulty of obtaining tungsten in a variety of conditions, the expense involved in machining and preparing the material for final testing, and the need for repetitive tests to determine the uniformity of behavior, the results are not as complete as would be desired. Some of the material available represented early attempts to fabricate large tungsten parts. Improvements in material quality have since been made. The extent of cracking of each type of material tested is shown in Fig. 9.

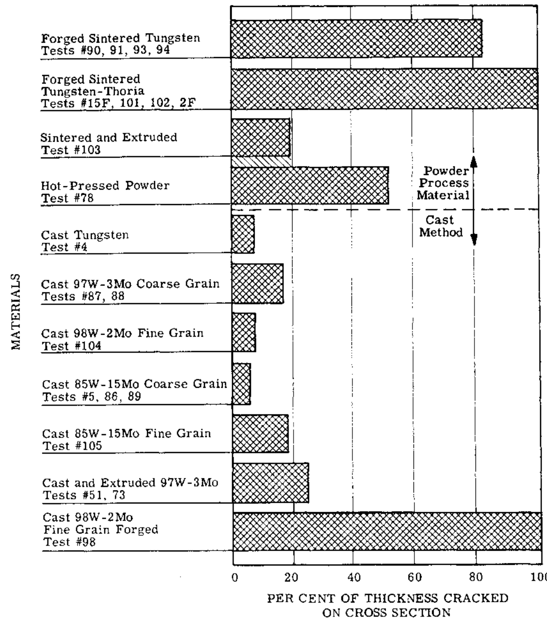

Fig. 9 Extent of cracking on cross section of fired tungsten nozzle.

In most cases, the fractures were not apparent upon visual examination after firing. Therefore, a cross section of each insert was examined microscopically to determine the extent of cracking. In most cases, the cracking was reported only for the cross section examined. Metallographic examination of the material was also conducted on this polished cross section. Unfortunately, it was not possible to similarly examine the material before the firing test. In the reporting of the crack length, there is no differentiation between cracks that formed during the firing cycle and cracks that formed during cool-down, because our examination procedure could not differentiate readily between these two types of cracks. However, since most of the cracks that were observed started on the cold side, it is believed that only a few cracks (that had clean fracture surfaces) occurred during cool-down.

Results for ten inserts made by *powder techniques* and processed to a density of 94% or more are given in Table 3. In four of these, the amount of deformation and the forging temperature were varied. The most crack resistant insert had been subjected to the lesser amount of hot reduction, 35%,

Table 3 Thermal-stress cracking results for powder-process tungsten nozzle inserts

Material and processing	Density, g/cm³	Grain size,[a] mils	Cracks observed	Grain growth
Tungsten,[b] sintered and forged 35% at 3250°F	18.0	15.0	one, 0.12 in.	moderate
35% at 2750	18.6	5.1	two, 0.4 in.	moderate
75% at 3250	19.0	1.5	two, 0.4 in.	considerable
75% at 2750	19.1	1.1	full fracture, plus one, 0.25 in.	moderate
$98W\text{-}2ThO_2$,[b] sintered and forged 35% at 3250°F				
35% at 2750	18.3	4.0	full fracture	negligible
35% at 2750	18.6	1.1	full fracture	negligible
75% at 3250	18.3	4.0	full fracture	negligible
75% at 2750	18.6	1.0	partial fracture	negligible
Tungsten,[c] sintered and extruded at 2350°F	18.0	1.3	one, 0.19 in.	extensive
Tungsten,[d] isostatically pressed at 2900°F	19.0	16.0	two, 0.25 in.	moderate

[a] Average grain size; does not include grain growth in throat section.
[b] Sintered material from General Electric Company, Cincinnati, Ohio; forged by Sifco, Cleveland, Ohio.
[c] Sintered material from General Electric Company, Cincinnati, Ohio; extruded by Canton Drop Forging and Manufacturing Company, Canton, Ohio.
[d] Powder from Allied Chemical Corporation, Morristown, New Jersey, pressed by Battelle Memorial Institute, Columbus, Ohio.

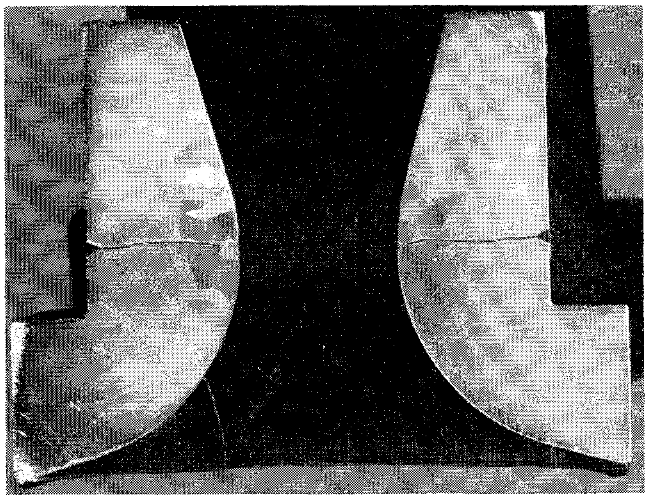

Fig. 10 Cross section of tungsten insert.

at the higher forging temperature, 3250°F. The other three test pieces cracked severely. All of these four inserts showed incipient grain growth at the throat, but the insert with the greatest amount of hot reduction at 3250°F showed the most grain growth. Figure 10 shows an etched cross section of this insert after exposure. The occurrence of the large grains is related to the strain induced by the forging operation, which is generally cold work (below the re-crystallization temperature) for tungsten, and the subsequent thermal cycle that occurred during firing. There is no indication that the growth of the large grains influenced the cracking that started on the outside surface and progressed inward. The presence of the crack in one of the large grains indicates that the grain had grown before the crack progressed through it.

The next four specimens in Table 3, which contained 2% thorium oxide, cracked more consistently; there was no indication of the effect of forging practice on the extent of cracking. However, there was very little grain growth at the throat section. Apparently, the presence of thoria increases cracking but inhibits grain growth.

The sintered and extruded test piece was obtained from an extrusion (made from a 9.2-in.-diam billet) that had cracked, but the test piece was machined from an uncracked portion. This insert cracked moderately during the test and showed substantial grain growth in the throat area with grain sizes up to $\frac{1}{8}$ in.

A hot-pressed insert made from 400-μ high-purity tungsten powder showed moderate cracking. Before firing, each 400-μ particle contained several hundred grains; after firing, there were from 6 to 30 grains in each particle. Figure 11 shows the interesting microstructure of the gas-side surface of this material after firing. The dark phase at the surface is believed to be a tungsten aluminate. The grain structure away from the face was similar through the section. For comparison, pressed and sintered tungsten of lower densities than the material described previously, tested under comparable conditions, would show more cracking and would be generally similar to that of the forged tungsten described previously.

Results for eleven *arc-cast tungsten inserts* are described in Table 4. Three of these materials were "hot worked." It can be noted that, with only one exception, the extent of cracking was significantly less than the cracking observed for the powder-process tungsten. Most of the cast material contained 2 to 15% molybdenum. These materials were selected, in part, because of the greater availability of the W-Mo alloys. Molybdenum exerts a grain-refining effect on tungsten, and the molybdenum alloys are preferred by the fabricators, because machining is less difficult and grain pull-out is minimized. There is no indication from the tests that the presence of 2 to 15% Mo affects the extent of thermal stress cracking.

It is interesting to note that the fine-grain material, such as that produced by the centrifugal casting process, generally showed more cracking than the coarse-grain material obtained from cold-mold casting techniques. In order to study the effect of grain orientation, inserts were machined in the longitudinal and in the transverse direction of a coarse grain ingot. The similar test results obtained indicate no substantial effect of grain orientation.

The "hot working" of W-Mo alloys did not significantly affect the extent of cracking. In the case of the forged 98W-2Mo fine-grain material, cracking was so severe that the results are inconsistent with the other test results. Unfortunately, insufficient detail was available on the processing to speculate about the reasons for the variance in performance of this particular test piece.

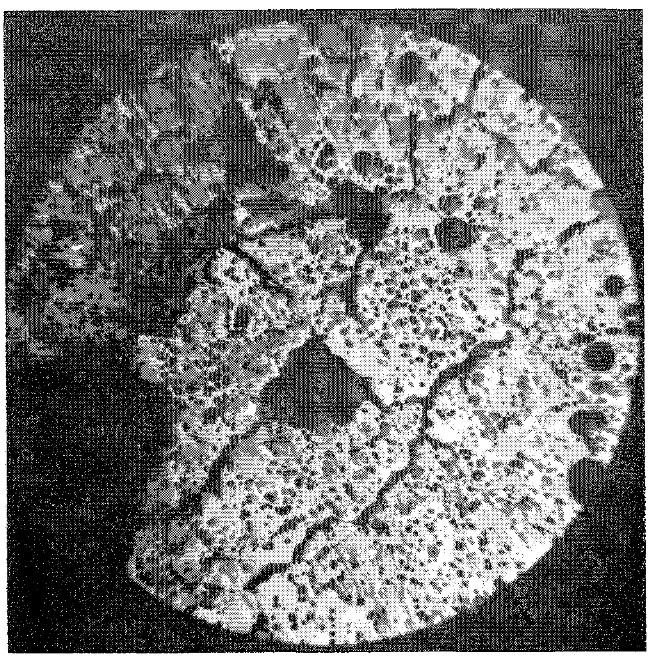

Fig. 11 Cross section of Thermit-cast tungsten after firing (×60). Note the absence of cracks at notch root and grain boundary phase.

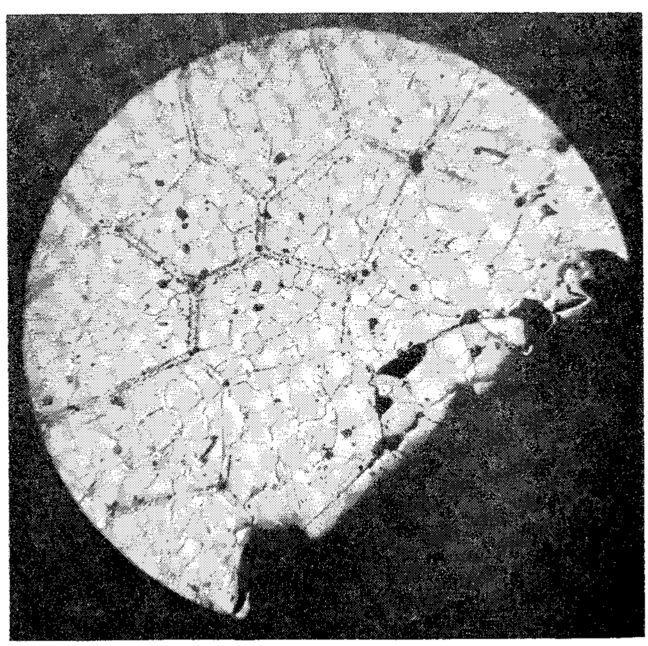

Fig. 12 Photomicrograph of cross section of hot-pressed tungsten showing the exposed gas-side (×75).

Table 4 Thermal-stress cracking results for cast tungsten nozzle inserts

Material	Source[a]	Grain size on section, in.	Cracks observed, outside, unless noted	Analysis C, ppm	Analysis O, ppm
Arc-cast tungsten	Climax	$\frac{3}{8} \times \frac{1}{16}$	one, $\frac{1}{16}$-in.	...	...
Arc-cast 97W-3Mo[b]	UC, CT	$\frac{1}{4} \times \frac{1}{8}$	one, $\frac{3}{8}$-in. four, $\frac{1}{8}$-in., hot side, intergran.	14	10
Centrif-cast 98W-2Mo	Oremet	$\frac{1}{16}$	one, $\frac{1}{16}$-in.	>20	>20
Arc-cast 85W-15Mo[b]	UC, CT	$\frac{1}{8} \times \frac{1}{4}$, long $\frac{1}{8}$, transverse	none one, $\frac{1}{8}$-in., intergran.	14	13
Arc-cast 85W-15Mo	Oremet	...	one, $\frac{1}{64}$-in.	...	...
Centrif-cast 85W-15Mo	Oremet	$\frac{1}{32}$	one, $\frac{3}{16}$-in.	80	>20
Arc-cast 97W-3Mo (4 in.) extr 1.77/1 at 2800°F	UC, Tapco	0.008	one, $\frac{1}{4}$-in.	15	18
Arc-cast 97W-3Mo (8 in.) extr 1.77/1 at 3000°F, forged 35% at 2740°F, stress-relieved 1650°F	UC, Du Pont, Sifco	$\frac{1}{32}$	two, $\frac{1}{8}$-in.	32	28
Centrif-cast 98W-2Mo forged 65%	Oremet	$\frac{1}{32}$	three, $\frac{1}{8}$-in.	50	50
Thermit-cast tungsten	Calarobic	0.012	one, $\frac{1}{4}$-in. (not std. insert)	...	...
Thermit-cast tungsten	Calarobic	$\frac{1}{16}$	none visible (not std. insert)	...	...

[a] Climax = American Metal Climax, Detroit, Michigan; UC = Universal Cyclops, Bridgeville, Pennsylvania; CT = Custom Tool, Minneapolis, Minnesota, Oremet = Oregon Metallurgical Corporation, Albany, Oregon; Tapco = Tapco Division, Thompson-Ramo-Wooldridge, Cleveland, Ohio; Du Pont, Baltimore; Maryland; Calarobic Incorporated, Pearl River, New York.
[b] Two inserts each from same ingot.

Two inserts cast by the Thermit reduction of tungsten oxide showed minimal cracking. Maximum available size of stock was $1\frac{1}{2}$-in. diam, so that the standard insert could not be used; the shoulder was omitted. Metallographic examination showed a dark discontinuous grain-boundary phase and a bright dispersed phase, some of which was also in the grain boundary in this material. Some of the grain boundary phase was aligned in such a way as to appear like a crack. The microstructure of this material at the root of the ground notch is shown in Fig. 12. The absence of cracks in this material is impressive.

Discussion of Results

Obviously, it is difficult to draw firm conclusions on the relative tendencies of different forms of tungsten to fracture under thermal stress in view of the limited number of test samples and the incomplete knowledge of the properties of the materials tested. The rate of motor-pressure build-up upon ignition would have a significant effect on the level of thermal stress and also would affect the rate of strain on the cold side of the tungsten insert. Efforts were made to maintain uniform start-up conditions but there were some unavoidable variations. However, there is no correlation between the extent of cracking and the observed minor variations in the motor pressure build-up.

There are at least five major variables among the materials tested: 1) chemistry, 2) method of consolidation, 3) the extent of hot or cold work, 4) the grain size, and 5) the ductile-to-brittle transition temperature. The first three variables largely determine the fourth and fifth, which in turn influence the mechanical properties. The third variable listed, the conditions of deformation, also influences the substructure, which in turn influences the mechanical properties. The data obtained on the extent of cracking do not indicate any significant effect related to the chemistry of the tungsten alloys. Many of the materials were of a high degree of purity. Alloying additions such as molybdenum exert substantial direct effects such as raising the temperature of re-crystallization and decreasing the grain size of cast material. Molybdenum additions will also likely raise the ductile-to-brittle transition temperature, as is common for solid-solution alloying additions to body-centered-cubic metals.

One of the important criteria of cracking should be the ductile-to-brittle transition temperature of the tungsten. All of the tungsten tested should be brittle at room temperature. At some temperature above 400°F, considerable ductility should be evidenced. Since it is indicated that the cracks initiate on the cold side of the nozzle insert from tensile stresses caused by the thermal gradient, it could be expected that the tungsten with the lowest transition temperature should show the least cracking.

Test data available from the Navy arc-cast tungsten program and from the literature[2, 3] on the transition temperatures of different forms of tungsten show considerable variation within a range of approximately 300° to 900°F. The lowest transition temperatures are obtained by cold-working tungsten to the extent that distinctly elongated grains are formed. The low transition temperature is then only attainable in the direction of grain elongation.[4] Available data indicate that the transition temperature of powder-process tungsten does not differ appreciably from that of arc-cast tungsten, the processing details being more influential in determining the transition temperature than is the method of consolidation. Data on forged tungsten-thoria alloy indicate a higher transition temperature[5] than for pure tungsten, although data for both materials varies widely depending on the extent of working. The data obtained in this program indicate that a correlation between the extent of cracking and the transition temperature may exist as one would expect, but sufficient data are not available to prove this correlation.

One firm conclusion from the test data is that coarse-grain materials show less cracking than the fine-grain materials. The large grain size of the arc-cast materials may well be largely responsible for the lesser amount of cracking they show. Even within a group of materials made by the same consolidation method, the materials of larger grain size showed less cracking than the fine grain size materials.

The suggestion that large grains improve the fracture resistance of metals is not in keeping with previous concepts. It has been established that higher strength and lower transition temperatures are associated with fine grain sizes for body-centered-cubic metals.[6] On the other hand, metals of large grain size are known to show relatively lower yield strengths than fine-grain metals.[7] The lower yield strength of the coarse-grain structure will permit plastic deformation to occur at a lower applied stress and may thereby minimize fracture. Single crystal tungsten is known to possess room temperature ductility. The large individual grains from arc-cast tungsten have demonstrated ductility at room temperature. Moreover, current theories of brittle fracture indicate that grain boundaries act as barriers for dislocation pileups and thereby permit stress concentrations and crack nucleation.[8] On this basis the large grain structure with fewer grain boundaries is expected to be less susceptible to brittle fracture.

Conclusions

Tungsten and high tungsten alloys have been found to be uniquely unaffected by chemical corrosion of solid-propellant exhaust gases of typical aluminum-containing propellants. Only in the case of highly oxidizing (nonmetallized) propellants is chemical reaction with the combustion gases a limiting problem. Coarse grain arc-cast tungsten has been found to be especially resistant to thermal stress fracture. Only tentative explanation of this behavior can be made from data currently available; further investigation is warranted to improve the understanding of the basic factors that control thermal fracture.

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