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# EFFECT OF WATER VAPOR/HYDROGEN ENVIRONMENTS ON COLUMBIUM ALLOYS

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Rocketdyne
A Division of North American Aviation, Inc.
Canoga Park, California

TECHNICAL REPORT AFML-TR-66-322
December 1966

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Air Force Materials Laboratory
Research and Technology Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

# NOTICES

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# FOREWORD

This report was prepared by the Materials Research Section, Research Division of Rocketdyne, a Division of North American Aviation, Inc., under United States Air Force Contract Number AF33(615)-2854. This contract was initiated under Project Number 7351, "Metallic Materials," Task Number 735101, "Refractory Metals."

The project was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, with Lt. L. D. Blackburn and Mr. L. D. Parsons acting as project engineers.

The authors wish to acknowledge the assistance of J. Mosher and J. Pero in conducting the tensile tests in $H_2O/H_2$ environments.

This report covers the period from 1 July 1965 to 30 June 1966. This report has been assigned the Rocketdyne identification number R-6573.

This report has been reviewed and is approved.

I. PERLMUTTER
Chief, Metals Branch
Metals and Ceramics Division
Air Force Materials Laboratory

# ABSTRACT

The results of an experimental investigation of the effect of water vapor/hydrogen environments on the mechanical properties of columbium and the B-66 columbium alloy are presented. Tensile tests were conducted on specimens of these materials in water vapor/hydrogen environments with $H_2O/H_2$ mixture ratios of 1 and 3.

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# INTRODUCTION

Columbium and columbium alloys have certain characteristics which make them quite attractive for use in such applications as advanced, regeneratively cooled rocket engine thrust chambers and ramjets which involve high heat fluxes and high temperatures. However, it has been established that under certain conditions, columbium and its alloys are susceptible to embrittlement and deterioration in the presence of hydrogen and water vapor/hydrogen mixtures. Because these environments will exist in the applications indicated above, it is necessary to evaluate the seriousness of this problem under the appropriate conditions.

There are published data showing that columbium is susceptible to hydrogen embrittlement at least below a temperature of 200 F. Recent work (Ref. 1) indicates that, under some conditions, embrittlement of columbium by hydrogen can occur at temperatures as high as 800 F. A program conducted at Rocketdyne indicated that a columbium alloy, B-66, also suffers loss of ductility from hydrogen at temperatures up to 800 F. There are only very limited data on the solubility and rate of hydrogen absorption into columbium at high hydrogen pressures. There were no previous data on the effect of water vapor/hydrogen mixtures on the mechanical properties of columbium.

Three primary areas will require investigation to accumulate the necessary information for the proper assessment of compatibility under simulated rocket engine and ramjet environments: (1) the effect of hydrogen at high pressures and elevated temperatures on mechanical properties, (2) the solubility and rates of absorption and desorption of hydrogen at high temperatures and high hydrogen pressures, and (3) the effect of water vapor/hydrogen environments on mechanical properties.

This report presents the results of an experimental investigation of the effect of water vapor/hydrogen environments on the mechanical properties of columbium and the B-66 columbium alloy.

[redacted]

## EXPERIMENTAL APPARATUS AND PROCEDURES

The effect of water vapor/hydrogen environments on the mechanical properties of columbium and the B-66 alloy was determined under conditions chosen to simulate, except for pressure, those to which materials would be exposed in hydrogen/oxygen fueled rocket or ramjet engines. Two $H_2O/H_2$ mixture ratios, 3 and 1, corresponding to the two limits currently used in hydrogen/oxygen engine operation were employed during these tests. These mixture ratios are on a volume basis. Figure 1 relates this mixture ratio, which will be used throughout this report because it gives a better indication of the actual environment involved, to the oxygen/hydrogen weight ratio which is more commonly used in presenting oxidizer/fuel ratios for propulsion systems

### MATERIALS

The materials used during this program were electron-beam melted columbium purchased from Fansteel Metallurgical Corp. and B-66 columbium alloy (Cb 5V-5Mo-1Zr) purchased from Westinghouse Electric Corp. Each of these materials was purchased in the form 0.030-inch-thick sheet for the tensile tests in water vapor/hydrogen environments.

Metallographic examination showed that the columbium sheet was in the recrystallized condition, and the B-66 alloy sheet was approximately one-half recrystallized. Chemistry and fabrication data for the materials are presented in Tables 1 and 2.

### APPARATUS

The tensile tests in water vapor/hydrogen environments were conducted in a Marshall tube furnace which has molybdenum disilicide heating elements and which was used in conjunction with a 60,000-pound Baldwin tensile testing machine.

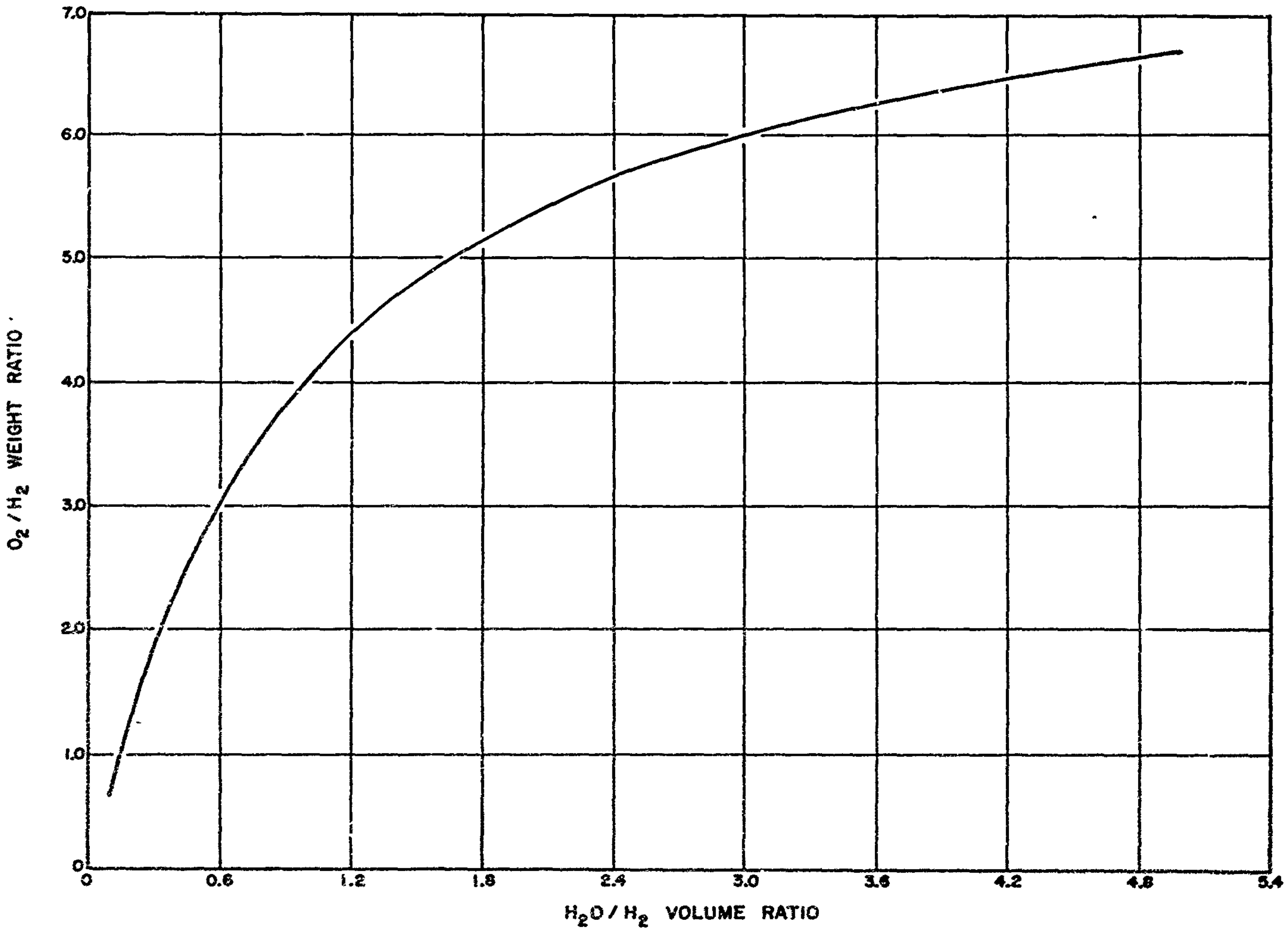

Figure 1. $O_2/H_2$ Weight Ratio in Terms of $H_2O/H_2$ Volume Ratio

# TABLE 1

## CHEMICAL COMPOSITION OF COLUMBIUM SHEET
(0.030-inch-thick sheet)

| Element | Chemical Analysis, ppm |
|---|---|
| C | 10 |
| O | 65 |
| N | 25 |
| H | 2 |
| Ta | 200 |
| W | 100 |
| Zr | 200 |
| Mo | 50 |
| Ti | 100 |
| Fe | 50 |
| Ni | 50 |
| Si | 50 |
| Mn | 20 |
| Ca | 10 |
| Al | 10 |
| Cu | 10 |
| Sn | 50 |
| Cr | 50 |
| V | 100 |
| Co | 50 |
| B | 2 |
| Cb | Balance |

## TABLE 2

## CHEMICAL COMPOSITION AND FABRICATION HISTORY OF B-66 COLUMBIUM ALLOY SHEET

(0.030-inch-thick sheet)

| Element | Chemical Analysis |
|---|---|
| Mo | 5.03 percent |
| V | 4.76 percent |
| Zr | 0.89 percent |
| O | 165 ppm |
| N | 74 ppm |
| C | 80 ppm |
| Cb | Remainder |

**Fabrication History Steps**

1. Double electron-beam melted and vacuum-arc remelted into 8-inch-diameter ingot
2. Extruded to 3- by 6-inch bar
3. Annealed at 1650 C
4. Forged to 1-1/2- by 9- by 18-1/2-inch slab
5. Annealed at 1550 C
6. Forged to 1- by 12- by 21-inch plate
7. Vacuum annealed at 1375 C
8. Warm rolled to 0.135-inch-thick sheet
9. Vacuum annealed at 1375 C
10. Warm rolled to 0.050-inch-thick sheet
11. Vacuum annealed at 1375 C
12. Cold rolled to 0.030-inch-thick sheet
13. Stress relieved at 985 C for 1 hour

A system, similar to that used by Battles (Ref. 2) was constructed for generating the water vapor/hydrogen mixtures. In addition, an apparatus for analyzing the water vapor/hydrogen mixture ratio has been added to the gas system. A method for analyzing the gas mixture was deemed necessary to ascertain that water vapor is not condensed in the cooler regions of the tensile furnace as well as to ensure that saturation is achieved in the constant-temperature bath.

A schematic representation of the water vapor/hydrogen testing system is shown in Fig. 2. Hydrogen used during these tests is purified by a catalytic De-oxo unit converting oxygen to water vapor. The water is collected in a desiccant and all impurities are reduced to less than 1 ppm total (Ref. 3) by collection in a molecular sieve at the temperature of boiling nitrogen.

The purified hydrogen flowrate is measured by a flowmeter, and is then bubbled into a presaturator containing an internally controlled heater and two external heaters. The water vapor/hydrogen mixture is then sent through the saturator which for tests performed at 1.00 $H_2O/H_2$ environment consisted of two bottles containing water and having frit entry ports and a third bottle for mist collection. These bottles were immersed in a precisely controlled constant-temperature bath. All the tubing transporting water vapor is heated with heating tapes. The generated water vapor/hydrogen mixture enters the tensile furnace at the top, then flows through the furnace and out the bottom.

Water is prevented from condensing in the Marshall tube furnace by pumping hot Dow Corning 200 fluid (230 to 250 F) through the pull rods and through the cooling coils protecting the O-rings from overheating at very high furnace temperatures.

To maintain a pure water vapor/hydrogen atmosphere, all the Buna-N O-rings in the Marshall furnace have been replaced by Viton A O-rings. The ball and socket joints in the water vapor/hydrogen apparatus are lubricated

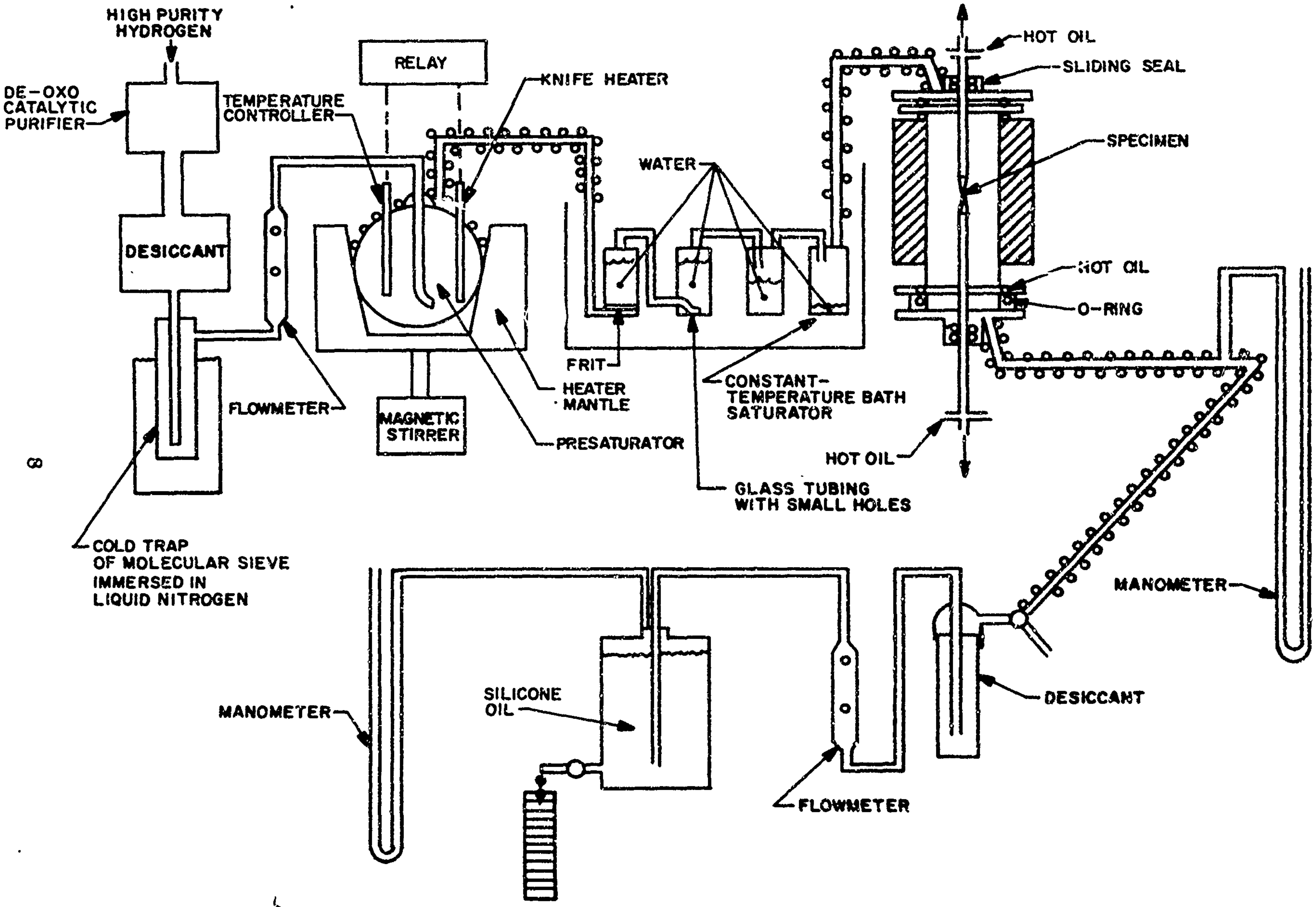

Figure 2. Schematic Representation of Water Vapor/Hydrogen Testing System

with Dow Corning silicone vacuum grease which has a vapor pressure of $5.8 \times 10^{-6}$ mm Hg ($7.62 \times 10^{-9}$ atmospheres) at 100 C. All the joints in the saturator are O-ring type containing Viton A O-rings. The temperature controller and knife heater are held in the presaturator with neoprene stoppers which have a vapor pressure of $1.1 \times 10^{-4}$ mm Hg ($1.45 \times 10^{-7}$ atmospheres) at 100 C.

Difficulty was encountered in obtaining the correct water vapor content in the gas for the $H_2O/H_2$ mixture ratio of 3. This difficulty was traced to the pressure drop across the two water-containing bottles of the constant-temperature bath. Such a pressure drop decreases the relative water content in the system. To reduce this pressure drop, the gas generating system was modified to include three bottles plus a mist collector in the constant-temperature bath. The first bottle contains a coarse frit; the second bottle contains, in place of the frit, glass tubing with small holes through which the gas passes. In the third bottle, the gas passes over the water instead of bubbling through it. The schematic representation of the system in Fig. 2, includes these changes.

For the $H_2O/H_2$ mixture ratio of 3, it was found necessary to adjust the temperature of the constant-temperature bath prior to each test because a small change in the barometric pressure causes an appreciable change on the water/hydrogen ratio. For example, an increase of barometric pressure from 740 to 745 mm Hg would decrease the $H_2O/H_2$ ratio from 3.00 to 2.92 if the constant-temperature bath setting was not changed accordingly. A similar change in the barometric pressure would reduce the 1.00 $H_2O/H_2$ mixture ratio to 0.987. This reduction was considered sufficiently small so that compensations for changes in barometric pressure were not required for the 1.00 mixture ratio.

Gas analysis consists of collection of water by a glass bottle filled with anhydrone [$Mg(ClO_4)_2$] which is weighed before and after to measure the water content. The water-free hydrogen is then passed through a flowmeter and the exact volume is measured by liquid displacement. Initially, water was used as the liquid medium but silicone oil was later substituted for water to eliminate the vapor pressure of the displacement liquid as a significant variable in this measurement. A manometer measures the hydrogen vapor pressure over the silicone oil in the liquid displacement bottle, so that the pressure is known and can be made the same at the finish of the measurement as at the start. The use of this manometer significantly reduced the scatter of the analyses. The pressure drop across the gas analyzer is also measured by a manometer. This information is needed for determining the theoretical $H_2O/H_2$ ratio obtained from the constant-temperature bath.

Analysis of the gases from the water vapor/hydrogen generating apparatus for the nominally $H_2O/H_2$ mixture ratio of 1.00 environment were made before and after entering the tensile furnace, and the analysis indicate that the $H_2O/H_2$ ratio varies within 1.00 ±0.05 for hydrogen flowrates between 233 and 363 cc/min. Therefore, from these tests there is no indication of water condensation in the cool furnace ends.

Because of the large density difference between hydrogen and water vapor, hydrogen may preferentially accumulate at the upper region of the furnace. If segregation occurs, it would be expected that a higher than normal water content would be evolved from the furnace until steady state was reached. To test this, an analysis was made 15 minutes after the 1 $H_2O/H_2$ vapor mixture entered the tensile furnace to replace argon at 400 F. The flowrate was such that during the 15-minute period of the $H_2O/H_2$ gas flow, the quantity of gas mixture passing through the furnace was equal to seven times the furnace volume. The results, however, did not indicate above-normal water content which would suggest that gas segregation is negligible. Furthermore, it is thought that the midpoint in the furnace, where the specimen is located, would have close to an average $H_2O/H_2$ vapor-gas mixture even if some gas segregation had occurred.

The possibility of gas segregation in the tensile furnace with the 3 $H_2O/H_2$ mixture ratio environment was tested by the same method as was used for the 1 $H_2O/H_2$ environment. An analysis was made 15 and 55 minutes after the

$H_2O/H_2$ mixture entered the tensile furnace to replace argon at 400 F. The results indicated mixture ratios of 3.3 and 3.02, respectively. A second series of analyses was conducted 15, 45, and 65 minutes after the $H_2O/H_2$ mixture entered the furnace and the results were 2.85, 2.86, and 2.98, respectively. The mixture ratios for the second series of tests were essentially within the 2.90 ±0.07 range that was being obtained from the $H_2O/H_2$ analyses at that time. On the basis of the second series of tests, it was concluded that there is no significant gas separation in the tensile test furnace.

Distilled water was used in the gas generating system for the tests on the B-66 alloy in the 1 and 3 $H_2O/H_2$ mixture ratio environments and on columbium in the 1 $H_2O/H_2$ mixture ratio environment. Prior to performing the tests on columbium in the 3 $H_2O/H_2$ mixture ratio environment, the system was cleaned and refilled with deionized-distilled water instead of the distilled water previously used. After refilling the system with deionized-distilled water, the manometer was installed for the first time on the liquid displacement bottle of the gas analysis apparatus.

Prior to performing the tests on the B-66 alloy in the nominally 3 $H_2O/H_2$ mixture ratio environment, the gas environment was analyzed as 2.90 ±0.07. The changes made before performing the tests on columbium resulted in a measured $H_2O/H_2$ mixture ratio of 3.00 ±0.03 which is near the limit of accuracy of the gas generating apparatus, which is determined by the ±0.5 F accuracy of the temperature measurements in the constant-temperature bath.

In summary, it was established that no significant separation of the hydrogen and water vapor occurred in the tensile furnace. The nominally 1.00 $H_2O_4$ mixture ratio environments had mixture ratios varying within 1.00 ±0.05. For the B-66 alloy, the nominally 3.00 $H_2O_2$ mixture ratio environments actually had mixture ratios of 2.90 ±0.07 while for pure columbium the mixture ratios were 3.00 ±0.03. For the remainder of this report the $H_2O/H_2$ environments will be referred to by their nominal values of 1 and 3.

## PROCEDURE

These tests were performed using approximately the same test sequence previously used (Ref. 4) to ascertain the compatibility of columbium and tantalum with hydrogen at 1 atmosphere of pressure. The specimens were heated to the test temperature in purified argon and the water vapor/hydrogen mixture was introduced after the temperature was stabilized. Following introduction of the water vapor/hydrogen atmosphere, a stress equal to 50 percent of the room-temperature yield strength of the specimens was applied. This stress corresponds to 48,800 and 20,250 psi for B-66 and columbium specimens, respectively. The stress was maintained for 30 minutes, and the specimen then was tested to failure at a relatively slow strain rate. This test sequence was designed to simulate some of the main features of actual engine operation. The preload during exposure to the $H_2O/H_2$ environment, at various test temperatures, is representative of stresses due to internal pressure in thrust chamber tubing for regeneratively cooled engines. The stress level in these tubes is nearly constant and of the same magnitude as used during the tests. Furthermore, the tubes extend from the combustion chamber, through the throat, and along the skirt of the engine, therefore experiencing a wide range of temperatures while exposed to an $H_2O/H_2$ environment. Many parts of the engine operate under conditions of temperature and stress which put them into the plastic region during firing. By using a very low strain rate, the specimens may be exposed to the $H_2O/H_2$ environment for reasonably long periods of time while undergoing plastic strain. The tensile tests were load paced at 120 lb/min or 16,000 psi/min for the 1/4 inch by 0.030 inch cross-section specimens. This load rate corresponded to a 0.001 in./in. min strain rate from 0 load to the yield point. The strain rate from the yield point to the ultimate strength was approximately 0.08 in./in. min for columbium and approximately 0.03 in./in. min for B-66. The length of time the specimens were in the plastic range was approximately 3 minutes for the columbium specimens and approximately 4 minutes for the B-66 specimens. Previous tensile tests in pure hydrogen conducted at Rocketdyne (Ref. 4) were performed at similar strain rates.

The temperature gradient over the 1-1/8-inch-long reduced section was ±3 F/linear inch during the 400 to 1500 F tests. The indicating thermocouple was located approximately 1/8 inch from the specimen near the center of the specimen, and this temperature was held within ±10 F during the test. Therefore, during the test, the temperature in the reduced section varied within ±13 F of the desired temperature.

The effect of previous exposure to hydrogen or "hydrogen activation" on the susceptibility of the materials to embrittlement from the $H_2O/H_2$ environment was also tested. The activation process used consisted of thermal cycling between 1500 and 900 F followed by outgassing in flowing inert gas at 1500 F. Previous work on columbium (Ref. 1) has shown that such treatment markedly affects the hydrogen absorption process, in fact, attainment of equilibrium solubility of hydrogen at temperatures below approximately 1100 F can only be attained in reasonable times in specimens which have undergone an activation treatment. The most significant feature of the activation process is the large difference in solubility of hydrogen at the upper and lower temperatures, so that thermal cycling will cause large quantities of hydrogen to be absorbed and desorbed. The upper temperature is probably not very critical because the solubility varies slowly with temperature above approximately 1400 F. In the vicinity of 900 F, however, the solubility changes rapidly with temperature. A slightly highe temperature would result in significantly less hydrogen absorption, and possibly less of an activation effect. The treatment used for the present work included three thermal cycles from 1500 to 900 F, with moderate heating and cooling rates and no hold time at the temperatures. At 900 F, after the third cycle, the hydrogen gas was replaced with helium, the specimen was heated to 1500 F, held for 0.5 hour to outgas, and furnace cooled. Typical weight gains of 10 to 20 ppm were noted; presumably part of this is oxygen, but even if it were all hydrogen, it would be a relatively small quantity.

Previous work (Ref. 4) has shown that this hydrogen activation heat treatment increased the degree of embrittlement which occurred during tests conducted in hydrogen on B-66 sheet specimens. Thermal cycling of a propulsion system by frequent engine starting could result in hydrogen activation when exposed to an $H_2O/H_2$ environment. If the material were protected by oxidation protection coatings, hydrogen absorption could occur although the coatings may protect against oxidation. Also, thermal cycling uncoated specimens between 1500 and 900 F may oxidize and thereby embrittle the specimens making it difficult to properly evaluate the actual test environment. Therefore, it was felt that for uncoated specimens activation by thermal cycling in hydrogen would better simulate actual propulsion conditions and enable better evaluation of the test results than would thermal cycling in $H_2O/H_2$ environment.

The design of the tensile specimens is shown in Fig. 3. The specimens were fabricated so that the longitudinal axis was parallel to the rolling direction.

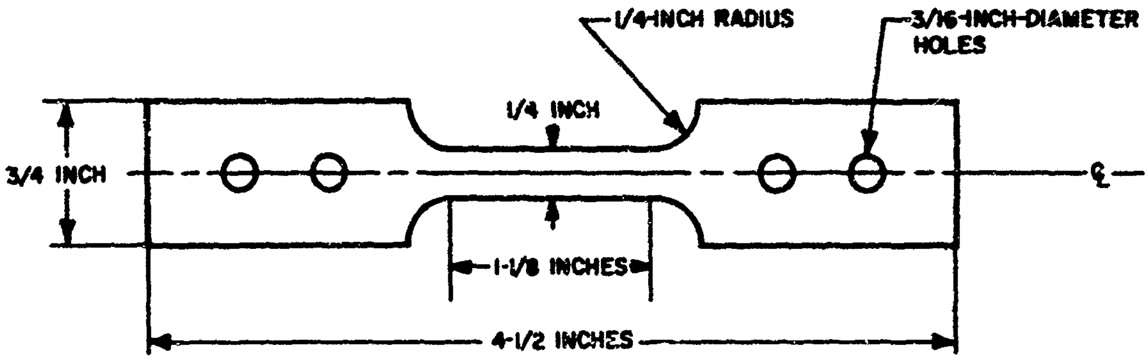

Figure 3. Tensile Specimen Design for Testing in Water Vapor/Hydrogen Environments

# RESULTS AND DISCUSSION

The results of mechanical tests performed on columbium and the B-66 columbium alloy in water vapor/hydrogen environments with $H_2O/H_2$ mixture ratios of 1 and 3 are tabulated in Tables 3 and 4. Table 5 contains the results of hydrogen and oxygen analyses performed on the tested specimens.

## EFFECT OF WATER VAPOR/HYDROGEN ENVIRONMENTS ON COLUMBIUM

The ductility of columbium specimens tested in $H_2O/H_2$ environments with mixture ratios of 1 and 3 are plotted in Fig. 4 and 5, respectively. The data indicate that there are two temperature regions of low ductility, one near 400 F and the other near 1050 F. The ductility minimum at 400 F occurs for tests conducted in an inert atmosphere as well as in the water vapor/hydrogen atmosphere. However, the ductility of the specimens tested in the 1 and 3 $H_2O/H_2$ environments was somewhat less than the ductility of the specimen tested in argon. There was no indication of oxidation during the 400 F tests and the hydrogen and oxygen absorption was also very low.

The percent elongation at 1050 F was approximately 20 for the tests in both $H_2O/H_2$ environments compared to 38-percent elongation obtained from tests performed in argon. The decrease of ductility at this temperature is accompanied by secondary cracking and surface oxidation. Secondary cracking refers to surface cracks that are formed in the reduced section, usually in the necked-down region near the fracture. The secondary cracks in the B-66 specimens are observable with the naked eye and appear parallel to the fracture surface. The oxygen contents absorbed by columbium during the tests at 1050 F were approximately 1350 and 900 ppm for the tests conducted in the 1 and 3 $H_2O/H_2$ environments, respectively. The hydrogen pickup was 109 ppm for tests in the 1 $H_2O/H_2$ environment and approximately 60 ppm for the 3 $H_2O/H_2$ environment.

# TABLE 3

## RESULTS OF TENSILE TESTS ON COLUMBIUM IN $H_2O/H_2$ AND INERT ENVIRONMENTS

| Specimen No. | Hydrogen Activated | Environment | Temperature, F | Ultimate Strength, psi | Yield Strength, psi | Percent Elongation(a) | Time in Environment, minutes | Weight Change, milligrams(b) | Surface Appearance | Comments |
|---|---|---|---|---|---|---|---|---|---|---|
| 152 | No | Air | Room | 56,400 | 39,400 | 36.0(c) | — | — | | |
| 153 | | | | 60,000 | 41,600 | 38.0(c) | — | — | | |
| 156 | | | | 54,300 | | — | — | — | | |
| 185 | | Argon | 400 | 53,900 | | 20.8 | — | +0.10 | NSO(d) | |
| 174 | Yes | | 400 | 56,800 | | 19.2 | — | No change | | |
| 183 | No | | 600 | 65,100 | | 27.2 | | +0.30 | | |
| 179 | | | 600 | 65,400 | | 24.7 | — | +0.40 | | |
| 180 | | | 1050 | 29,100 | | 38.2 | — | +0.08 | | |
| 181 | | | 1500 | 16,400 | | 66.6 | — | +0.01 | | |
| 151 | | $H_2O/H_2$ = 1.00 | 400 | (e) | | 15.1 | 51 | (f) | | Held 30 minutes at 40,250 psi |
| 158 | | | 400 | 55,000 | | 15.5 | 60 | (f) | | |
| 170 | Yes | | 400 | 54,100 | | 15.5 | 52 | +0.01 | | Specimen chemically cleaned after activation |
| 171 | Yes | | 400 | 54,600 | | 18.6 | 52 | No change | | |
| 166 | No | | 600 | 68,200 | | 28.6 | 56 | +1.20 | | |
| 165 | No | | 600 | 71,200 | | 28.8 | 60 | (f) | | |
| 172 | Yes | | 600 | 66,400 | | 31.1 | 52 | +0.91 | | |
| 154 | No | | 800 | (e) | | 28.2 | 55 | (f) | | No oxidation in reduced section; some oxidation in grip area |
| 169 | No | | 1050 | 30,200 | | 20.3 | 60 | +6.1 | Light tan | Secondary cracking |
| 173 | Yes | | 1050 | 32,300 | | 18.8 | 53 | +8.97 | Light blue-tan | Secondary cracking; specimen chemically cleaned after activation |
| 155 | No | | 1200 | (e) | | 30.6 | 65 | (f) | Gray | |
| 157 | | | 1500 | 5,200 | | 43.1 | 23 | (f) | Dark gray | |
| 182 | | $H_2O/H_2$ = 3.00 | 400 | 55,200 | | 16.7 | 52 | +0.03 | NSO | |
| 183 | | | 600 | 65,100 | | 27.2 | 52 | +0.30 | NSO | |
| 177 | | | 800 | 37,400 | | 25.7 | 50 | +3.1 | Light tan | |
| 184 | | | 1050 | 29,000 | | 23.2 | 51 | +6.75 | Light gray | Secondary cracking |
| 175 | | | 1050 | 29,800 | | 18.3 | 53 | +5.31 | Light gray | Secondary cracking |
| 186 | | | 1200 | 21,400 | | 39.2 | 26 | +8.57 | Dark gray | Broke during 1/2-hour hold at 50 percent of room temperature yield strength |
| 176 | | | 1200 | 27,800 | | 54.7 | 51 | +13.20 | Dark gray | |
| 178 | | | 1500 | 15,100 | | 50.7 | 18 | +25.5 | Dark purple | Broke during 1/2-hour hold at 50 percent of room temperature yield strength |
| 167 | | | 1500 | 15,300 | | 53.1 | 51 | +36.5 | Dark purple | Held 1/2-hour at 10,000 psi instead of 20,250 psi |

(a) Percent elongation over 1-1/8-inch length
(b) Total weight of columbium and B-66 specimens is approximately 9 grams
(c) Percent elongation over 1.0-inch length
(d) No sign of oxidation
(e) No ultimate strength obtained
(f) No measurement made

## TABLE 4

## RESULTS OF TENSILE TESTS ON B-66 COLUMBIUM ALLOY IN $H_2O/H_2$ ENVIRONMENTS

| Specimen No. | Hydrogen Activated | Environment | Temperature, F | Ultimate Strength, psi | Percent Elongation[a] | Time in Environment, minutes | Weight Change, milligrams[b] | Surface Appearance | Comment |
|---|---|---|---|---|---|---|---|---|---|
| 145 | No | Argon | 1200 | 105.700 | 9.3 | — | 1.10 | NSO | |
| 146 | No | Argon | 1500 | 104,900 | 16.8 | — | ·0.69 | NSO | |
| 147 | No | $H_2O/H_2$ = 1.00 | 400 | 104,600 | 20.8 | 56 | +0.01 | NSO[c] | |
| 101 | No | ↓ | 400 | 91,600 | 18.6 | 47 | (d) | ↓ | Specimen tested in the fully recrystallized condition |
| 119 | Yes | ↓ | 400 | 98,500 | 12.4 | 54 | (d) | ↓ | Specimen chemically cleaned after activation |
| 120 | ↓ | ↓ | 400 | 108,800 | 12.8 | 70 | (d) | ↓ | |
| 121 | ↓ | ↓ | 500 | 102,400 | 17.8 | 52 | (d) | ↓ | |
| 122 | ↓ | ↓ | 500 | 106,700 | 17.3 | 52 | (d) | ↓ | |
| 148 | No | ↓ | 800 | 102,000 | 10.3 | 55 | +0.72 | Light gray | |
| 149 | ↓ | ↓ | 800 | 100,600 | 12.8 | 55 | +0.83 | Light gray | |
| 150 | ↓ | ↓ | 800 | 101,700 | 11.8 | 55 | +0.70 | Light gray | |
| 102 | ↓ | ↓ | 800 | 89,700 | 14.1 | 52 | (d) | Faint oxidation | Specimen tested in the fully recrystallized condition |
| 127 | ↓ | ↓ | 1200 | 95,500 | 10.6 | 66 | (d) | Purple-tan | |
| 128 | ↓ | ↓ | 1500 | 92,9[illegible] | 3.1 | 56 | (d) | Dark blue | |
| 129 | ↓ | ↓ | 1500 | 88,300 | 4.1 | 50 | (d) | Dark blue | |
| 134 | ↓ | $H_2O/H_2$ = 3.00 | 400 | 102,200 | 17.3 | 52 | −0.07 | NSO | |
| 141 | ↓ | ↓ | 400 | 100,300 | 18.3 | 54 | +0.08 | ↓ | Specimen tested in the fully recrystallized condition |
| 123 | Yes | ↓ | 400 | 100,900 | 19.9 | 57 | −0.22 | ↓ | |
| 124 | Yes | ↓ | 400 | 103,100 | 17.7 | 54 | −0.10 | ↓ | |
| 125 | Yes | ↓ | ,00 | 101,500 | 20.0 | 53 | +0.01 | ↓ | Mist collector overflowed during test, $H_2O$ content probably high |
| 139 | No | ↓ | 800 | 99,500 | 11.4 | 51 | +3.70 | ↓ | |
| 136 | ↓ | ↓ | 800 | 100,600 | 10.6 | 53 | +0.85 | ↓ | |
| 135 | ↓ | ↓ | 1100 | 97,900 | 9.8 | 52 | +5.45 | Light gray | |
| 131 | ↓ | ↓ | 1100 | 98,300 | 11.1 | 55 | +6.50 | Light tan | |
| 133 | ↓ | ↓ | 1200 | 96,500 | 6.2 | 51 | +10.81 | Light brown | Secondary cracking |
| 137 | ↓ | ↓ | 1200 | 95,600 | 9.3 | 51 | +9.83 | Purple brown | Secondary cracking |
| 140 | ↓ | ↓ | 1200 | 89,500 | 4.0 | 53 | +10.20 | Gray | Only a small amount of secondary cracking; specimen tested in the fully recrystallized condition |
| 142 | ↓ | ↓ | 1200 | 88,700 | 4.5 | 53 | +11.25 | Light brown | Secondary cracking; specimen tested in the fully recrystallized condition |
| 130 | ↓ | ↓ | 1500 | 90,200 | 2.2 | 54 | +37.3 | Purple gray with cracking | |

(a) Percent elongation over 1-1/8-inch length
(b) Total weight of columbium and B-66 specimens is approximately 9 grams
(c) No sign of oxidation
(d) No measurement made

## TABLE 5

## HYDROGEN AND OXYGEN CONTENTS IN COLUMBIUM AND B-66 COLUMBIUM ALLOY SPECIMENS AFTER TESTING IN $H_2O/H_2$ ENVIRONMENTS

| Specimen Number | Material | Condition of Specimen | Hydrogen Activated | Test Conditions | | Gas Analysis | | Absorbed During Test | | Ratio of Oxygen Absorbed to Hydrogen Absorbed | Hydrogen Plus Oxygen Absorbed by Analysis, ppm | Weight Gain, grams | Final Weight, grams | $\frac{\text{Weight Gain}}{\text{Final Weight}} \times 10^{-6}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $H_2O/H_2$ Ratio | Temperature, F | Oxygen, ppm | Hydrogen, ppm | Oxygen, ppm | Hydrogen, ppm | | | | | |
| 152 | Columbium | As Received | | | | 662 | 8 | | | | | | | |
| 152c | ↓ | Chemically Cleaned | | | | 632 | 13 | | | | | | | |
| 153 | ↓ | As Received | | | | 707 | 8 | | | | | | | |
| 153c | ↓ | Chemically Cleaned | | | | 741 | 8 | | | | | | | |
| 156 | ↓ | As Received | | | | 404 | 12 | | | | | | | |
| 156c | ↓ | Chemically Cleaned | | | | 197 | 10 | | | | | | | |
| 175 | ↓ | As Received | | | | 685 | 9 | | | | | | | |
| | Average | As Received | | | | 615 | 9 | | | | | | | |
| | Average | Chemically Cleaned | | | | 523 | 10 | | | | | | | |
| 170 | Columbium | Chemically Cleaned | Yes | 1.00 | 400 | 618 | 10 | 95 | 0 | — | 95 | +0.00001 | 7.90500 | 1 |
| 165 | ↓ | Chemically Cleaned | No | ↓ | 600 | 688 | 11 | 165 | 1 | 165 | 166 | — | — | — |
| 166 | ↓ | Chemically Cleaned | No | ↓ | 600 | 741 | 14 | 218 | 4 | 54 | 222 | +0.00120 | 9.43234 | 127 |
| 154 | ↓ | Chemically Cleaned | No | ↓ | 800 | 888 | 9 | 365 | - | — | 365 | — | — | — |
| 173 | ↓ | Chemically Cleaned | Yes | ↓ | 1050 | 1874 | 119 | 1351 | 109 | 12 | 1460 | +0.008975 | 8.781065 | 1020 |
| 155 | ↓ | Chemically Cleaned | No | ↓ | 1200 | 2907 | 498 | 2384 | 488 | 5 | 2872 | — | — | — |
| 157 | ↓ | Chemically Cleaned | No | ↓ | 1500 | 3754 | 358 | 3231 | 348 | 9 | 3579 | — | — | — |
| 182 | ↓ | Chemically Cleaned | No | 3.00 | 400 | 659 | 14 | 136 | 4 | 34 | 140 | 0.00003 | 9.65565 | 3 |
| 183 | ↓ | Chemically Cleaned | No | ↓ | 600 | 335 | 53 | — | 43 | — | 43 | 0.00030 | 9.33595 | 32 |

# TABLE 5
(Continued)

| Specimen Number | Material | Condition of Specimen | Hydrogen Activated | Test Conditions | | Gas Analysis | | Absorbed During Test | | Ratio of Oxygen Absorbed to Hydrogen Absorbed | Hydrogen Plus Oxygen Absorbed by Analysis, ppm | Weight Gain, grams | Final Weight, grams | Weight Gain / Final Weight x $10^{-6}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $H_2O/H_2$ Ratio | Temperature, F | Oxygen, ppm | Hydrogen, ppm | Oxygen, ppm | Hydrogen, ppm | | | | | |
| 177 | Columbium | Chemically Cleaned | No | 3.00 | 800 | 1119 | 24 | 596 | 14 | 42 | 610 | 0.00310 | 9.35370 | 330 |
| 175 | | Chemically Cleaned | No | | 1050 | 1407 | 54 | 884 | 44 | 20 | 928 | 0.00531 | 8.48205 | 630 |
| 184 | | Chemically Cleaned | No | | 1050 | 1455 | 69 | 932 | 59 | 16 | 991 | 0.00675 | 9.27015 | 730 |
| 186 | | Chemically Cleaned | No | | 1200 | 1488 | 78 | 965 | 68 | 14 | 1033 | 0.00857 | 9.59095 | 880 |
| 176 | | Chemically Cleaned | No | | 1200 | 949 | 153 | 426 | 143 | 3 | 569 | 0.01320 | 9.57379 | 1380 |
| 178 | | Chemically Cleaned | No | | 1500 | 2138 | 202 | 1615 | 192 | 8 | 1807 | 0.02550 | 9.0719 | 2810 |
| 167 | | Chemically Cleaned | No | | 1500 | 1703 | 216 | 1180 | 206 | 6 | 1386 | 0.03650 | 8.71795 | 170 |
| 143 | B-66 | As Received | | | | 129 | 1 | | | | | — | — | — |
| 101* | | Chemically Cleaned | No | 1.00 | 400 | 210 | 7 | 81 | 6 | 13 | 87 | — | — | — |
| 147 | | Chemically Cleaned | No | | 400 | 103 | 4 | — | 3 | — | — | +0.000001 | 9.33922 | 1 |
| 119 | | Chemically Cleaned | Yes | | 400 | 360 | 8 | 231 | 7 | 33 | 238 | — | — | — |
| 121 | | Chemically Cleaned | Yes | | 500 | 160 | 8 | 31 | 7 | 4 | 38 | — | — | — |
| 102* | | Chemically Cleaned | No | | 800 | 240 | 12 | 111 | 11 | 10 | 122 | — | — | — |
| 149 | | Chemically Cleaned | No | | 800 | 232 | 16 | 103 | 15 | 7 | 118 | +0.00083 | 9.18826 | 91 |
| 148 | | Chemically Cleaned | No | | 800 | 171 | 11 | 42 | 10 | 4 | 52 | +0.00072 | 9.42690 | 76 |
| 127 | | Chemically Cleaned | No | | 1200 | 610 | 69 | 481 | 68 | 7 | 549 | — | — | — |
| 128 | | Chemically Cleaned | No | | 1500 | 3960 | 436 | 3831 | 435 | 9 | 4266 | — | — | — |

*Specimen recrystallized

## TABLE 5

## (Concluded)

| Specimen Number | Material | Condition of Specimen | Hydrogen Activated | Test Conditions | | Gas Analysis | | Absorbed During Test | | Ratio of Oxygen Absorbed to Hydrogen Absorbed | Hydrogen Plus Oxygen Absorbed by Analysis, ppm | Weight Gain, grams | Final Weight, grams | $\frac{\text{Weight Gain}}{\text{Final Weight}} \times 10^{-6}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $H_2O/H_2$ Ratio | Temperature, F | Oxygen, ppm | Hydrogen, ppm | Oxygen, ppm | Hydrogen, ppm | | | | | |
| 125 | B-66 | Chemically Cleaned | Yes | 3.00 | 400 | 90 | 7 | — | 6 | — | — | 0.00001 | 8.74737 | 1 |
| 141* | | Chemically Cleaned | No | | 400 | 170 | 2 | 41 | 1 | 41 | 42 | 0.00008 | 9.20620 | 9 |
| 134 | | Chemically Cleaned | No | | 400 | 147 | 5 | 18 | 4 | 4 | 22 | 0.00007 | 9.32075 | 8 |
| 139 | | Chemically Cleaned | No | | 800 | 187 | 8 | 58 | 7 | 8 | 65 | 0.00370 | 9.40775 | 390 |
| 135 | | Chemically Cleaned | No | | 1100 | 692 | 60 | 563 | 59 | 9 | 622 | 0.00545 | 9.34785 | 580 |
| 137 | | Chemically Cleaned | No | | 1200 | 860 | 87 | 731 | 86 | 8 | 817 | 0.00983 | 9.41265 | 1040 |
| 142* | | Chemically Cleaned | No | | 1200 | 1097 | 103 | 968 | 102 | 9 | 1070 | 0.01125 | 9.29290 | 1210 |
| 130 | | Chemically Cleaned | No | | 1500 | 2868 | 307 | 2739 | 306 | 9 | 3045 | 0.0373 | 9.3458 | 3990 |

*Specimen recrystallized

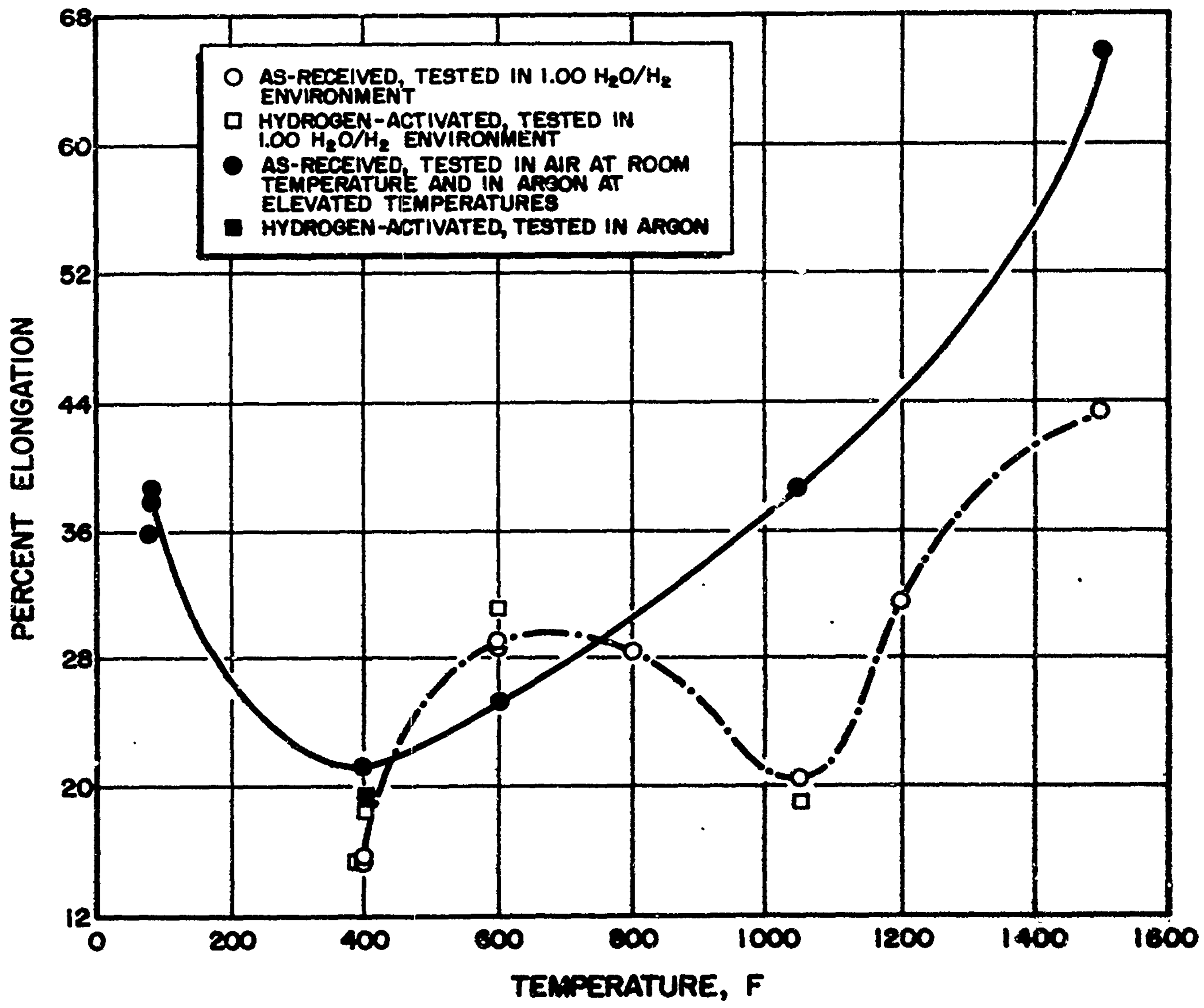

Figure 4. Ductility of Columbium as a Function of Temperature in $H_2O/H_2$ Environments With a $H_2O/H_2$ Mixture Ratio of 1.00

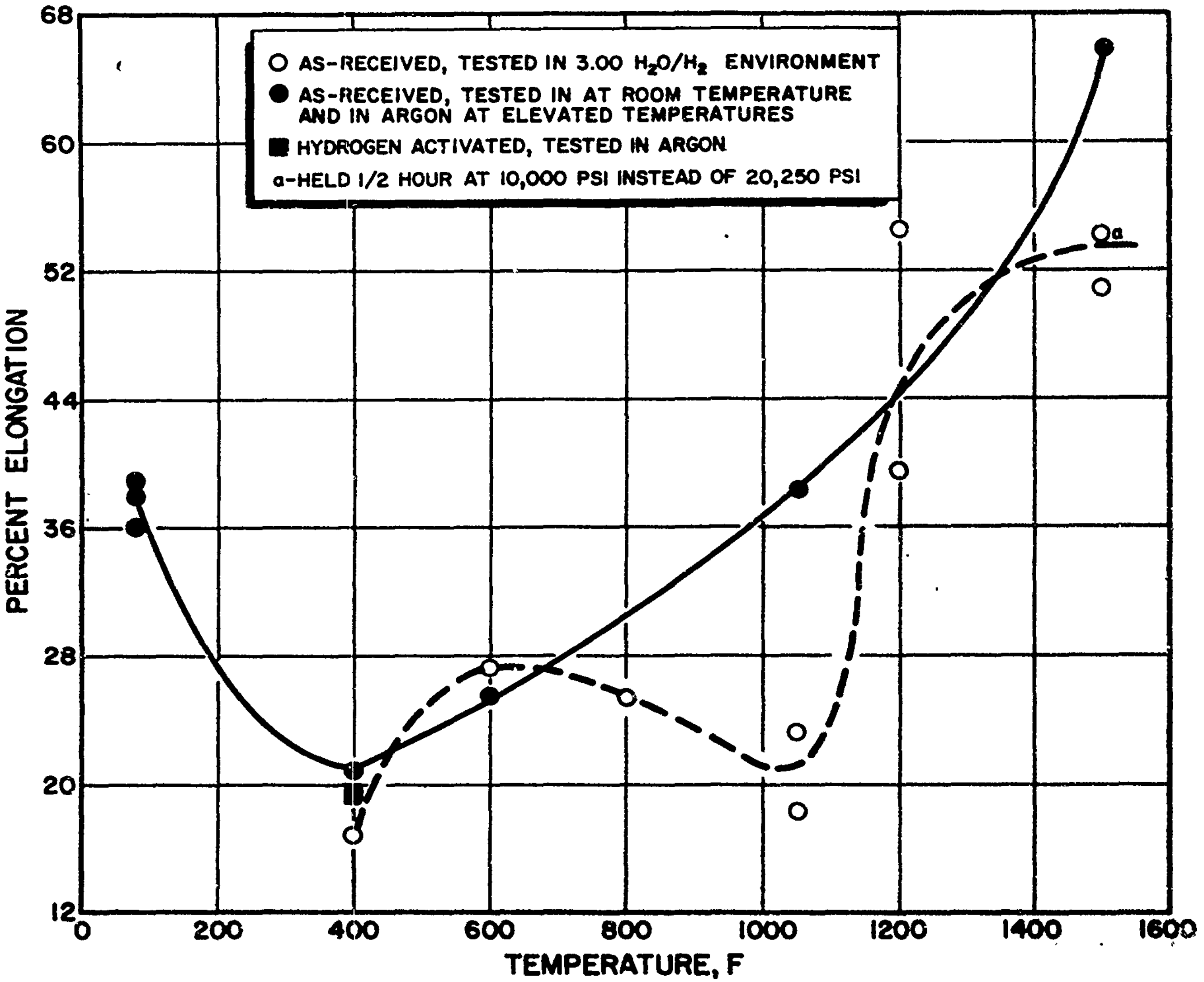

Figure 5. Ductility of Columbium as a Function of Temperature in $H_2O/H_2$ Environments With Mixture Ratio of 3.00

The ductility increased with increasing temperature above 1050 F, but was somewhat lower at 1200 and 1500 F for tests conducted in the 1 $H_2O/H_2$ environment than for tests conducted in argon. For tests conducted at 1200 F in the 3 $H_2O/H_2$ environment, the data displayed some scatter but the ductility was definitely higher than for tests at this temperature in the 1 $H_2O/H_2$ environment. At 1500 F in the 3 $H_2O/H_2$ environment, the decrease in ductility from tests conducted in argon was approximately half as large as the decrease for tests in the 1 $H_2O/H_2$ environment. Appreciable surface discoloration and oxygen and hydrogen absorption resulted from the 50- to 60-minute exposure to the $H_2O/H_2$ environments, but the oxide coating that was formed was quite adherent, more adherent than oxide coatings formed in air at these temperatures.

To more closely simulate actual engine operating conditions, all specimens were brought to test temperature, exposed to the test environment, and then subjected, for 0.5 hour, to a preload of 50 percent of the room temperature yield strength, or 20,250 psi. This stress was found to be higher than the ultimate strength of columbium at 1500 F, so the first specimen tested at this temperature failed during application of the preload. As a check on the validity of data obtained during this 1500 F test, another test was performed wherein the preload was limited to 10,000 psi (for 0.5 hour) after which the specimen was loaded to failure at the normal strain rate. The strength and elongation values from this latter test agreed with the values from the test under similar conditions in which failure occurred during preload application. The weight gain in the specimen preloaded to 10,000 psi was greater because of the longer time of exposure to the water vapor/hydrogen environment.

Tests performed at 400, 600, and 1050 F in the 1 $H_2O/H_2$ environment on specimens which had previously been hydrogen activated showed that the activation heat treatment had no effect on the ductility. Earlier work (Ref. 4) had shown a decrease in ductility for activated columbium specimens tested in pure hydrogen (1 atmosphere). Because this adverse effect on ductility was eliminated by reducing the hydrogen pressure to the 0.5 atmosphere of the 1 $H_2O/H_2$ mixture, it was concluded that no effect would be observed at a hydrogen pressure of 0.25 atmosphere, i.e., with the

3 $H_2O/H_2$ mixture. In addition, hydrogen activation was not found to reduce the ductility of B-66 specimens when tested in the 3 $H_2O/H_2$ environment although it had reduced with the 1 $H_2O/H_2$ environment. Therefore, no activated columbium specimens were tested in the 3 $H_2O/H_2$ environment.

The tensile strength of specimens tested in the $H_2O/H_2$ environments with mixture ratios of 1.00 and 3.00 are plotted in Fig. 6 and 7, respectively. The highest strength was found in specimens tested at 600 F. Above 600 F, the strength decreased from approximately 66,000 psi at 600 F to 15,000 psi at 1500 F. There was no significant effect of the environment on the strength.

Metallographic examination was made of a series of columbium specimens tested in the 1 $H_2O/H_2$ environment. Sections intersecting the fracture surfaces are shown in Fig. 8 through 11 of specimens tested at 400, 1050, 1200, and 1500 F, respectively. The fracture at 400 F is quite ductile with a very high reduction of area, although the elongation is only 15.5 percent. Surface cracking is readily observable in the fractures at 1050 and 1200 F, and this cracking apparently had an important role in effecting a reduction of ductility as measured by percent elongation at these temperatures. Secondary cracking did not occur at 1500 F although oxidation by water vapor during the test caused the surfaces to become irregular.

The columbium-hydride phase was observed only in the columbium specimen tested at 1050 F. This phase appears as a needle-like Widmanstatten second-phase on the surface of the specimen shown in Fig. 12. Experience at Rocketdyne with columbium which contains hydrogen indicates that this phase is columbium hydride, based on its structure and response to the lactic-HF-HNO, etchant. The hydride phase forms on cooling below 350 F, which is the highest temperature at which the hydride phase can exist (Ref. 5). Therefore, the hydride phase was not present during the tensile test. However, the presence of the hydride phase at the surface after testing indicates that the hydrogen content at the surface must have been greater than 645 ppm which is the limit of hydrogen solubility in columbium at room temperature (Ref. 5).

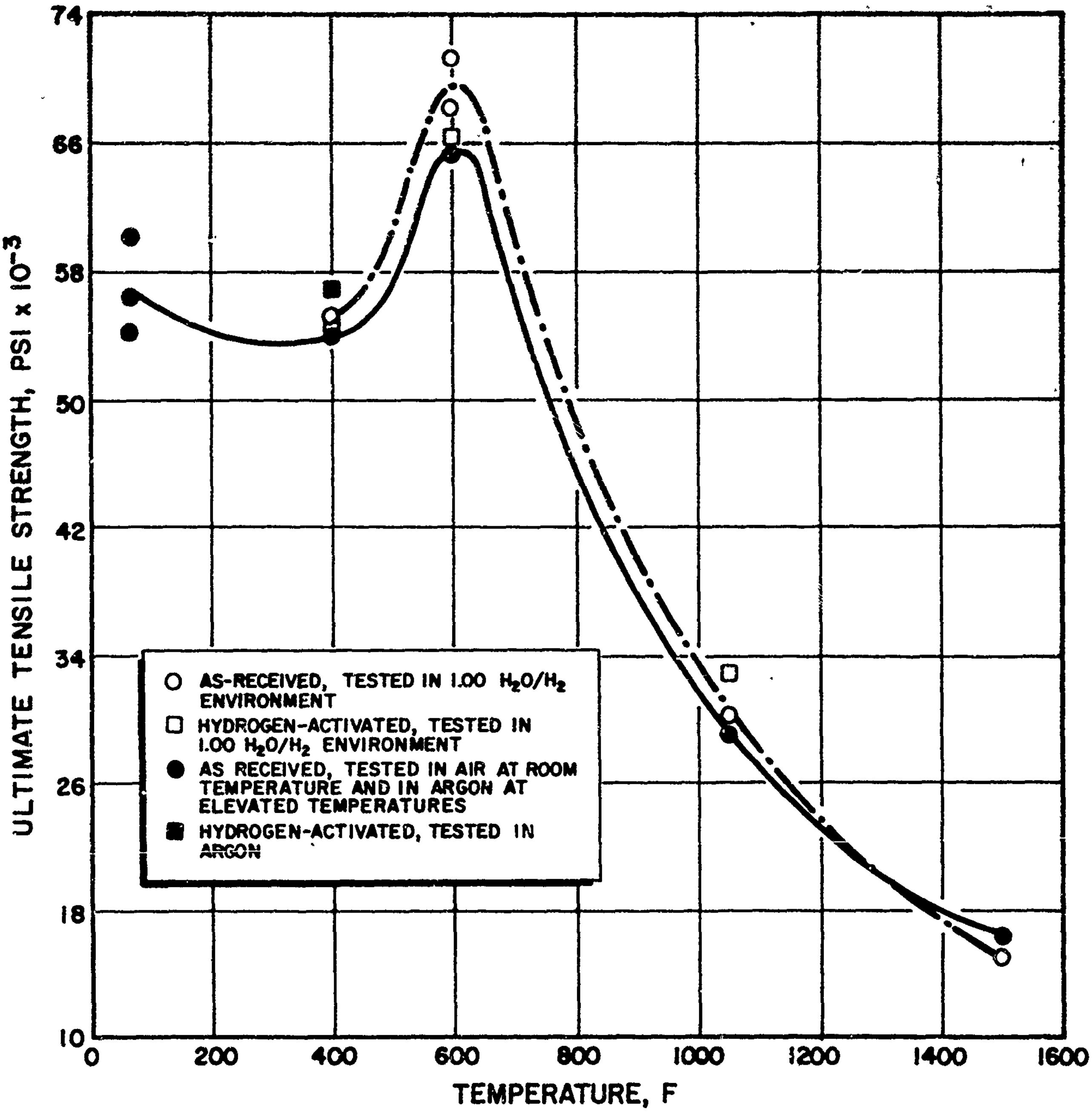

Figure 6. Ultimate Tensile Strength of Columbium as a Function of Temperature in $H_2O/H_2$ Environments With Mixture Ratio of 1.00

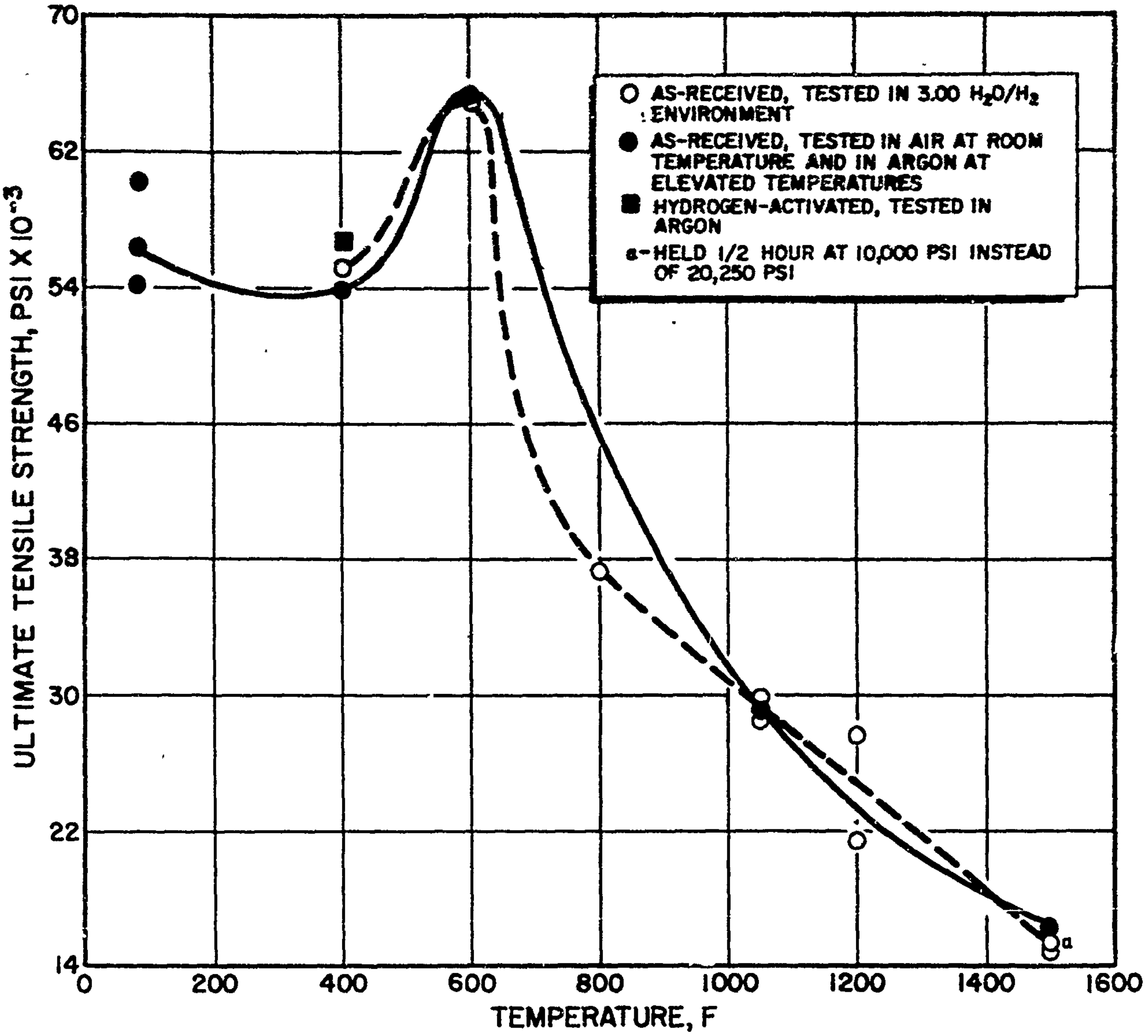

Figure 7. Ultimate Tensile Strength of Columbium as a Function of Temperature in $H_2O/H_2$ Environments With Mixture Ratio of 3.00

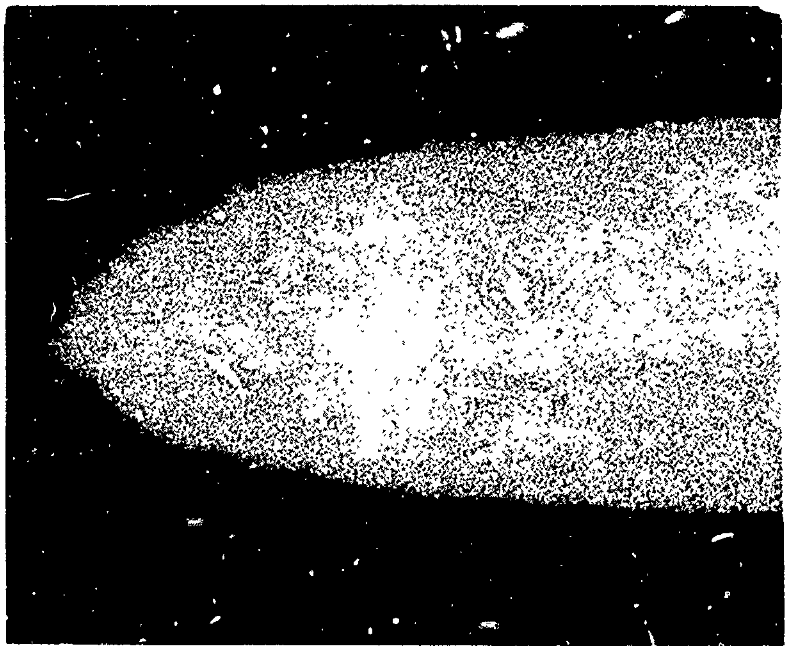

Figure 8. Columbium Specimen No. 170, Tested in 1.00 $H_2O/H_2$ Environment at 400 F, 15.5-Percent Elongation, Unetched, 100X

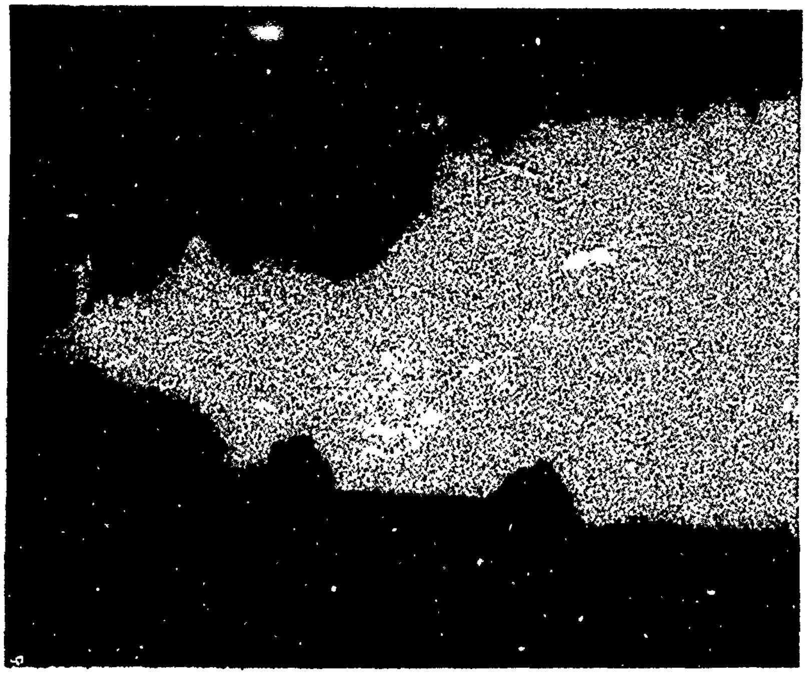

Figure 9. Columbium Specimen No. 173, Tested in 1.00 $H_2O/H_2$ Environment at 1050 F, 18.8-Percent Elongation, Unetched, 100X

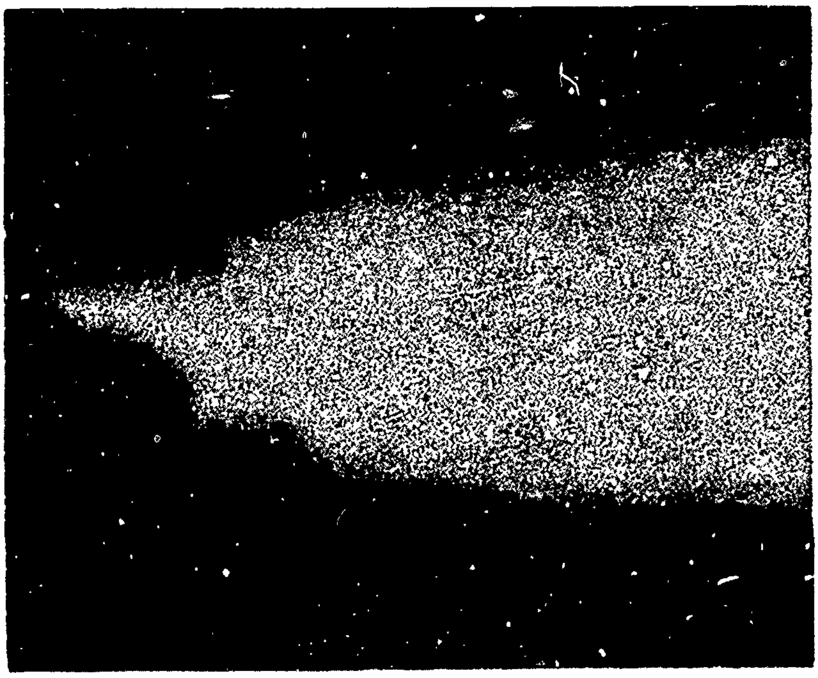

Figure 10. Columbium Specimen No. 155, Tested in 1.00 $H_2O/H_2$ Environment at 1200 F, 30.6-Percent Elongation, Unetched, 100X

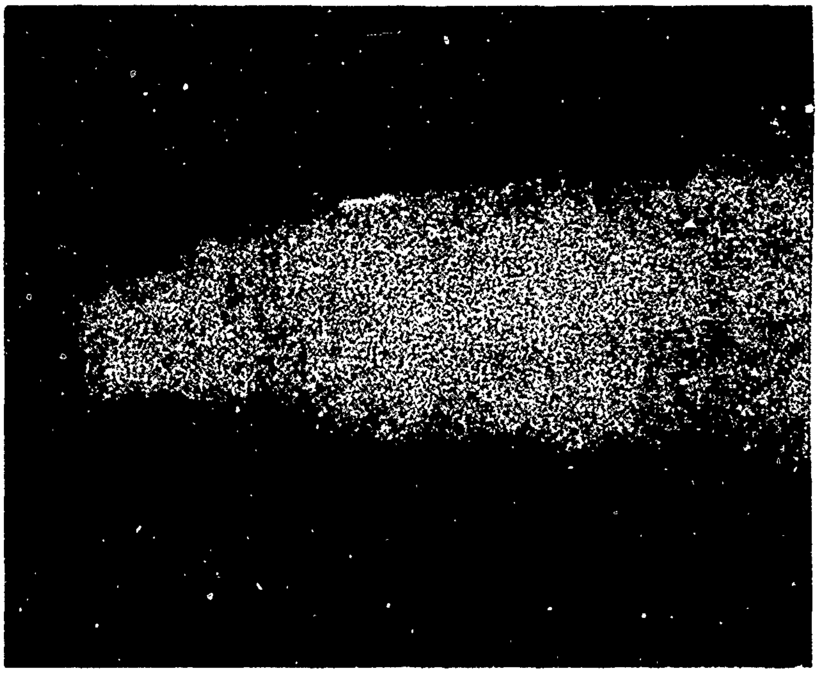

Figure 11. Columbium Specimen No. 157, Tested in 1.00 $H_2O/H_2$ Environment at 1500 F, 43.1-Percent Elongation, Unetched, 100X

Figure 12. Columbium Specimen No. 173, Tested in $1.00\ H_2O/H_2$ Environment at 1050 F (Etchant: 30 Lactic-10 HF-1 $HNO_3$) 500X

The maximum hydrogen content found by analysis in the columbium specimens tested at 1050 F was 119 ppm. The presence of the hydride phase at the surface indicates that the hydrogen must have been largely concentrated at the surface. Even during the tensile test there must have been a higher hydrogen concentration at the surface than at the interior of the specimen, because loss of hydrogen during cooling would lower somewhat the hydrogen content at the surface. Because the hydride phase was observed only in specimens tested at 1050 F and because surface cracking was most severe at 1050, it is assumed that the surface cracking is related to the relatively high surface hydrogen contents.

Figures 13 and 14 reveal the presence of a thin oxide phase at the surface of specimens tested at 1200 and 1500 F. A porous, dark, second oxide layer was also present on the surface of the specimen tested at 1500 F. There was no indication of a hydride phase in these specimens although the hydrogen content obtained from tests performed at 1500 F was as high as 498 ppm. This is higher than the hydrogen concentration in specimens tested at 1050 F although still below the hydrogen solubility limit. Therefore, the lack of hydride formation on cooling to room temperature would indicate that any hydrogen which may have concentrated at the surface during the test diffused into the interior during cooling.

A series of columbium specimens were analyzed by vacuum fusion analysis for oxygen and hydrogen after the tensile tests in the $H_2O/H_2$ environments. Parts of three specimens which were tested at room temperature in air were analyzed in the as-received and in the chemically cleaned condition for base line data. The results indicate that chemical cleaning reduced the oxygen content on an average about 100 ppm and increased the hydrogen content about 1 ppm. Because the specimens were all chemically cleaned prior to testing in the $H_2O/H_2$ environments, the average oxygen and hydrogen contents in chemically cleaned specimens were subtracted from the analyzed contents to obtain the amount of oxygen and hydrogen absorbed during the tests.

The results given in Table 5 of hydrogen and oxygen analyses for the columbium specimens show for tests conducted at 400 to 800 F in the

1 $H_2O/H_2$ environment that oxygen absorption was fairly low and hydrogen absorption was probably too low to significantly affect mechanical properties From 1050 to 1500 F, the oxygen and hydrogen contents increased significantly from 1874 to 3754 ppm for oxygen and from 109 to 348 ppm for hydrogen. The oxygen and hydrogen contents were somewhat higher for specimens tested at 400 to 800 F in the 3 $H_2O/H_2$ environment than in the 1 $H_2O/H_2$ environment. However, at 1050 F and above, the quantities of oxygen and hydrogen absorbed were considerably greater in the 1 $H_2O/H_2$ environment than in the 3 $H_2O/H_2$ environment.

When columbium or B-66 alloy specimens react with the $H_2O/H_2$ environments, both oxygen and hydrogen may be absorbed as a result of reaction with the $H_2O$, and hydrogen may be absorbed as a result of direct reaction with the $H_2$. The hydrogen released by the reaction with $H_2O$ is atomic hydrogen and should be relatively easily and rapidly absorbed. On the other hand, the molecular hydrogen must dissociate into atomic hydrogen through chemical adsorption onto the specimen surface before the hydrogen can be absorbed. Obviously, the ratio by weight of the oxygen absorbed to the hydrogen absorbed (if all the hydrogen evolved is absorbed) as a result of the reaction with $H_2O$ is 8. The column in Table 5 giving the ratio of oxygen absorbed to hydrogen absorbed was included as a possible aid in determining the source of the hydrogen absorbed, i.e., whether it came mainly from reaction with $H_2O$ or mainly from reaction with the $H_2$.

Unfortunately, an unambiguous determination of the source of the absorbed hydrogen is not possible because of other complicating factors. For example, hydrogen may be evolved during cooling of the specimen after a test. Walter and Offner (Ref. 6) have shown that hydrogen evolution occurs in flowing argon above 900 F. Following tensile testing in the water vapor/hydrogen atmosphere, the specimens were cooled to below 200 F in purified argon before removing from the furnace. It is, therefore, possible that at least some of the hydrogen absorbed in tests conducted above 900 F was evolved on cooling before the specimens had cooled below the temperature range in which significant hydrogen evolution could occur. On the other hand, for the tests conducted above 900 F, the oxide formed on the surface during the test would tend to inhibit hydrogen desorption.

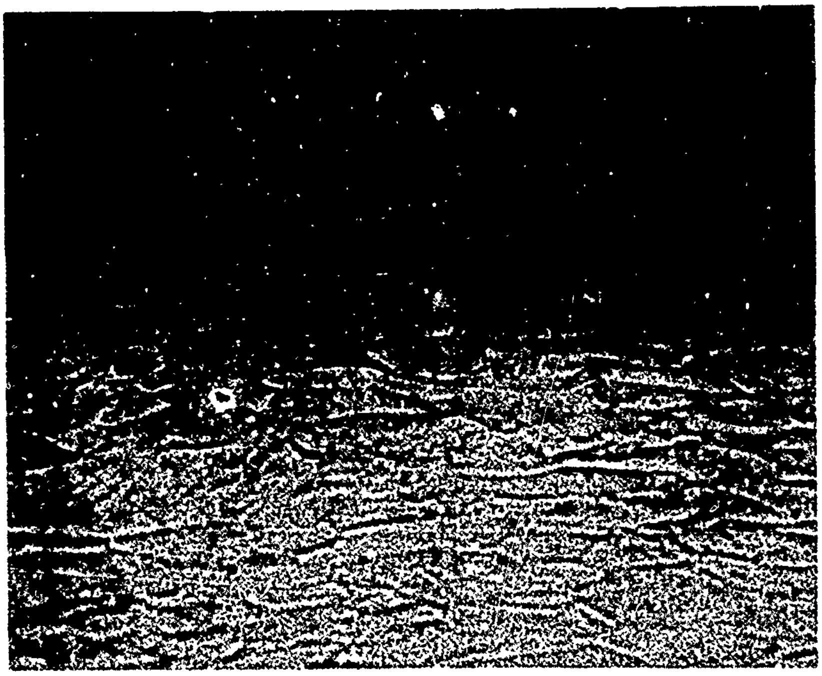

Figure 13. Columbium Specimen No. 155, Tested in 1.00 $H_2O/H_2$ Environment at 1200 F (Etchant: 50 Lactic-2 HF-30 $HNO_3$) 500X

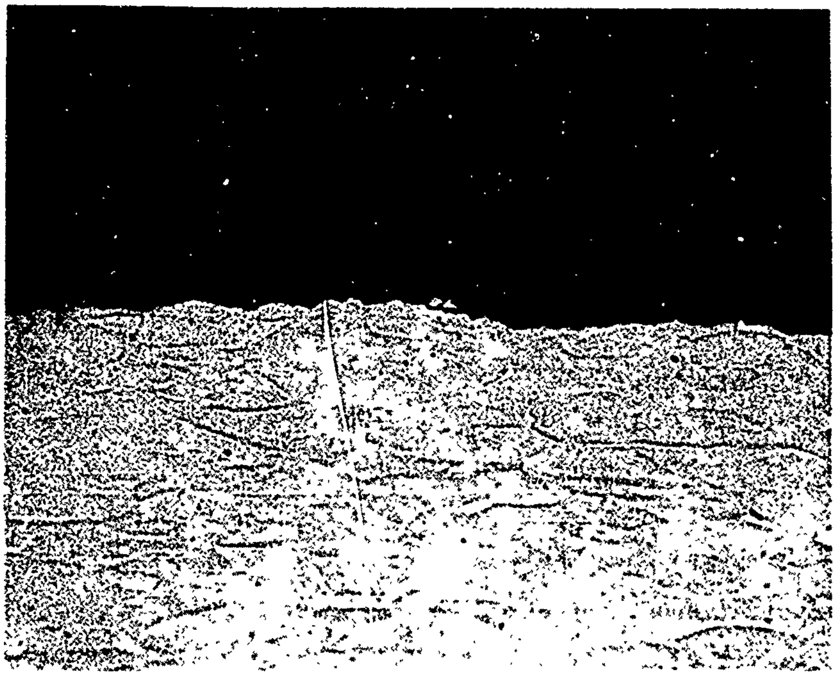

Figure 14. Columbium Specimen No. 157, Tested in 1.00 $H_2O/H_2$ Environment at 1500 F (Etchant: 50 Lactic-2 HF-30 $HNO_3$) 500 X

A second problem that can occur is loss of oxide during sampling. If the sum of hydrogen and oxygen absorption is less than the weight change of the specimen before and after testing, oxide loss during sampling would be suspected. The weight change during the tests is included in Table 5 to make this comparison. The weight change should not be construed as representative of the interstitial absorption in the fracture region of the specimen. This is because the specimen is partially protected from oxidation in the grip region and also the temperature is lower and applied stress less outside the notch or reduced sections.

To summarize, hydrogen absorption can occur from reaction with the water vapor and from reaction with hydrogen. The oxygen analysis gives a measure of the amount of atomic hydrogen released at the metal surface by the reaction with the water vapor. It seems resonable to assume that the major portion of any atomic hydrogen released at the metal surface will be absorbed into the metal rather than undergo recombination to form molecular hydrogen. In that case, if the amount of hydrogen absorbed in the metal is equal to or less than the amount of atomic hydrogen released during the reaction with the water vapor, i.e., if the ratio of oxygen absorbed to hydrogen absorbed is greater then 8, then the hydrogen absorbed must come predominantly from reaction with the water vapor.

The ratio of oxygen absorbed to hydrogen absorbed is higher than 8 for all of the columbium specimens analyzed which were tested at temperatures less than 1200 F. Three of the six specimens tested at 1200 and 1500 F had lower ratios of O/H absorbed than 8. The interstitial absorption during the test was, however, greater by weight change measurements than by vacuum fusion analyses over this temperature range which would indicate oxide loss during sampling. Therefore, on the basis of these data, hydrogen absorption in columbium would appear to be predominantly from reaction with water vapor over the entire temperature range. The oxide formed during tests at 1200 and 1500 F was thicker than that formed at lower temperatures and thus was more easily removed during sampling. At lower temperatures there was a much closer relationship between the hydrogen and oxygen absorbed, as determined by analysis, and the weight gain.

The higher oxygen absorption resulting from tests at temperatures above 1050 F in the 1 $H_2O/H_2$ environment compared to tests in the 3 $H_2O/H_2$ environment would certainly not be expected. The 358- and 216-ppm hydrogen contents at 1500 F in the 1 and 3 $H_2O/H_2$ environments, respectively, was perhaps related to the solubility limit of hydrogen in columbium in contact with 1/2 and 1/4 atmosphere hydrogen partial pressure for the 1 and 3 $H_2O/H_2$ environments, respectively, if it is assumed that hydrogen evolution can occur through the surface oxide layer at this temperature. The hydrogen solubility in columbium in contact with 1/2 and 1/4 atmosphere hydrogen pressure at 1500 F is about 390 ppm and 250 ppm, respectively, as determined by Albrecht, et al. (Ref. 7 ).

Duplicate samples were analyzed from tests conducted at 1050 and 1200 F in the 3 $H_2O/H_2$ environment, and the results indicate no evident relationship between the amount of oxygen and hydrogen absorbed and embrittlement.

## EFFECT OF WATER VAPOR/HYDROGEN ENVIRONMENTS ON THE B-66 COLUMBIUM ALLOY

The ductility of B-66 specimens tested in $H_2O/H_2$ environments with mixture ratios of 1 and 3 are plotted in Fig. 15 and 16, respectively. The data indicate that a small decrease of ductility occurred due to the water vapor/hydrogen atmosphere at 800 F for the 1 $H_2O/H_2$ environment and at 400 and 800 F for the 3 $H_2O/H_2$ environment. The ductility at 1200 F was decreased due to the 3 $H_2O/H_2$ environment but not the 1 $H_2O/H_2$ environment and at 1500 F there was substantial embrittlement in both $H_2O/H_2$ environments. Embrittlement at 1200 F in the 3 $H_2O/H_2$ environment is associated with secondary cracking. Therefore, the $H_2O/H_2$ atmospheres reduced the ductility of the alloy at temperatures between 400 and 1500 F except for the tests performed at 400 and 1200 F in the 1 $H_2O/H_2$ environment and at 1100 F in the 3 $H_2O/H_2$ environment. The 3 $H_2O/H_2$ atmosphere resulted in greater embrittlement in all cases compared to the 1 $H_2O/H_2$ atmosphere.

Included in the data are three fully recrystallized specimens (No. 140, 141, and 142) which were tested in the 3 $H_2O/H_2$ environment and two fully

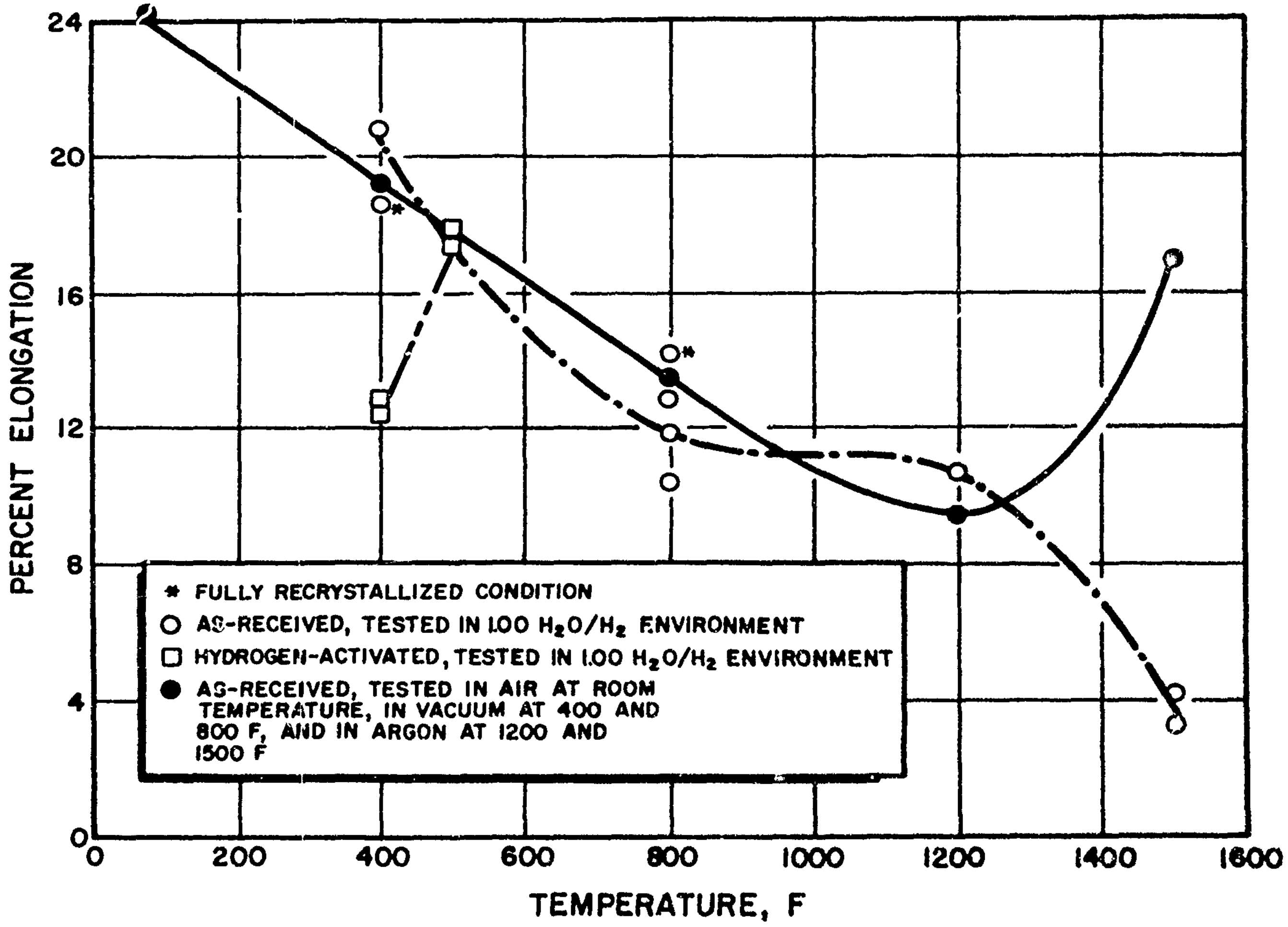

Figure 15. Ductility of B-66 Alloy as a Function of Temperature in $H_2O/H_2$ Environments With a Mixture Ratio of 1.00

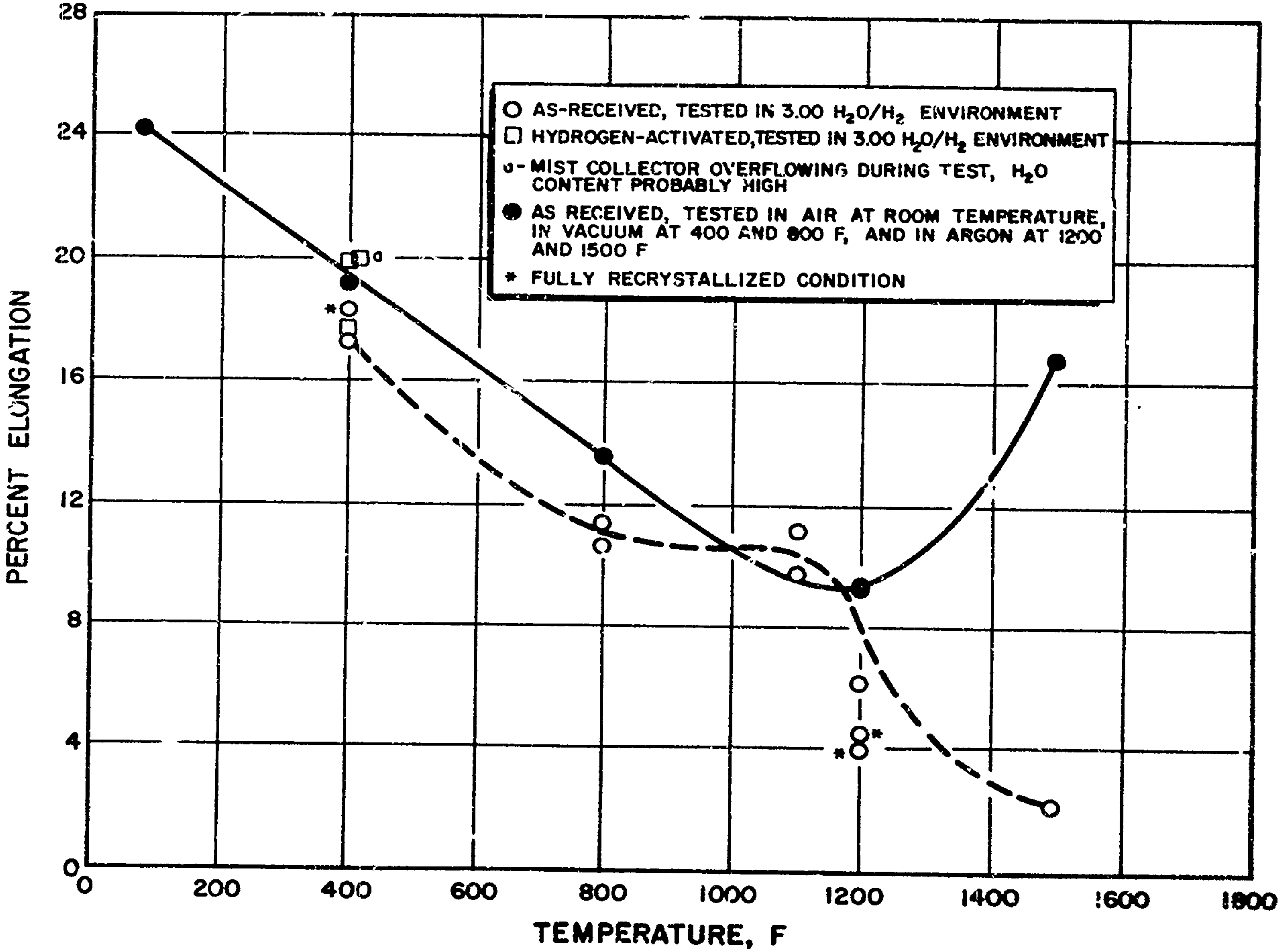

Figure 16. Ductility of B-66 Alloy as a Function of Temperature in $H_2O/H_2$ Environments With a Mixture Ratio of 3.00

recrystallized specimens (No. 101 and 102) tested in the 1 $H_2O/H_2$ environment. The two fully recrystallized specimens tested at 1200 F in the 3 $H_2O/H_2$ atmosphere had substantially lower ductility than the wrought specimens.

Hydrogen activation prior to testing effected nearly a 50-percent reduction of ductility at 400 F in the 1 $H_2O/H_2$ environment. However, there was essentially no decrease of ductility caused by activation for specimens tested at 500 F in the 1 $H_2O/H_2$ environment or at 400 F in the 3 $H_2O/H_2$ environment. Tests performed during a previous program (Ref. 4) in pure hydrogen on similarly hydrogen activated B-66 alloy specimens of similar design indicated that a reduction of ductility occurred because of the hydrogen atmosphere at temperatures from 400 F to 800 F, and the ductility in hydrogen at 400 F was less than the ductility in the 1 $H_2O/H_2$ atmosphere at 400 F. Therefore, it appears that diluting the hydrogen with 1/2 atmosphere water vapor acted to somewhat suppress embrittlement caused by hydrogen at 400 F and eliminated this effect at elevated temperatures. Also, the 1/4 atmosphere hydrogen and 3/4 atmosphere water vapor partial pressures of the 3 $H_2O/H_2$ environment did not embrittle activated specimens of the B-66 alloy even at 400 F.

The low hydrogen concentration (8 ppm) of the hydrogen activated specimens which were embrittled at 400 F in the 1 $H_2O/H_2$ environment suggests that embrittlement was a surface phenomenon rather than resulting from hydrogen in solution. Embrittlement of the B-66 alloy activated specimens and the columbium specimens at 400 F could best be explained on the basis of a surface-type reaction occurring from lowering of the surface energy of a newly formed crack by chemical adsorption of hydrogen onto the crack surface. On the other hand, activation is apparently not entirely a surface phenomenon, because removal of the surface layer by chemical cleaning with $HNO_3/HF$ did not remove the effect of activation for one of the specimens tested at 400 F.

The embrittlement of the B-66 alloy at temperatures above 400 F is evidently caused by oxygen as is evidenced by the decrease of ductility with increasing $H_2O/H_2$ ratio. Associated with the very low ductility at 1500 F is oxide formation which is shown in Fig. 17 and 18 for specimens tested at 1200 and 1500 F, respectively. The oxide phase is readily observable in both photomicrographs and was a significant proportion of the specimen shown in Fig. 18.

The effect of an oxide layer on the mechanical properties of the B-66 alloy has not been determined. However, the presence of a comparable oxide layer on Ta-10W has been found in a previous study (Ref. 4) to result in a substantial decrease of ductility. It is thought that, because of the similarity of the materials, a relatively thick surface oxide on the B-66 alloy such as shown in Fig. 17 and 18 could account for the embrittlement encountered during the 1200 and 1500 F tests in the $H_2O/H_2$ environment. The fact that a hydride phase is not evident in Fig. 17 and 18 may not be too significant. The authors have not been able during previous studies of B-66 specimens charged with hydrogen to metallographically observe the hydride phase, although considerable effort was made to do so. In any case, it is believed that embrittlement of B-66 alloy at 1200 and 1500 F can be explained solely on the basis of embrittlement caused by the oxide.

The oxygen content in the B-66 specimens tested at 1500 F is about the same as in the columbium specimens tested at 1500 F. The fact that these B-66 specimens have a much thicker oxide layer would suggest that the solubility of oxygen in B-66 is less than in columbium at 1500 F. The difference in oxygen solubility may explain the difference in embrittlement of the two metals at this temperature.

The tensile strength of B-66 alloy specimens tested in the 1 and 3 $H_2O/H_2$ environments are shown in Fig. 19 and 20, respectively. The data for the inert environment are taken from tests in air at room temperature, in vacuum at 400 and 800 F, and in argon at 1200 and 1500 F. Although the data appear discontinuous, they agree fairly well with literature data obtained from tests in vacuum between room temperature and 1500 F. For some reason there is less change in strength with temperature for tests performed in the $H_2O/H_2$ environments than for tests performed in inert environments. There may, however, be a slight decrease of strength at 1500 F caused by oxidation which accompanies the embrittlement observed

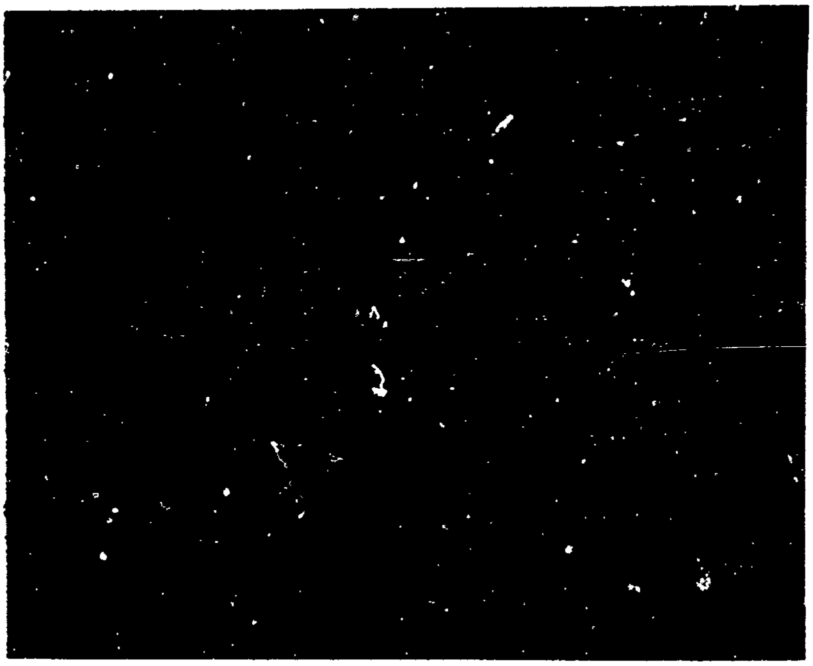

Figure 17. Specimen No. 127 Tensile Tested at 1200 F in Water Vapor/Hydrogen Environment With a Mixture Ratio of 1.00; Not Etched; 100X

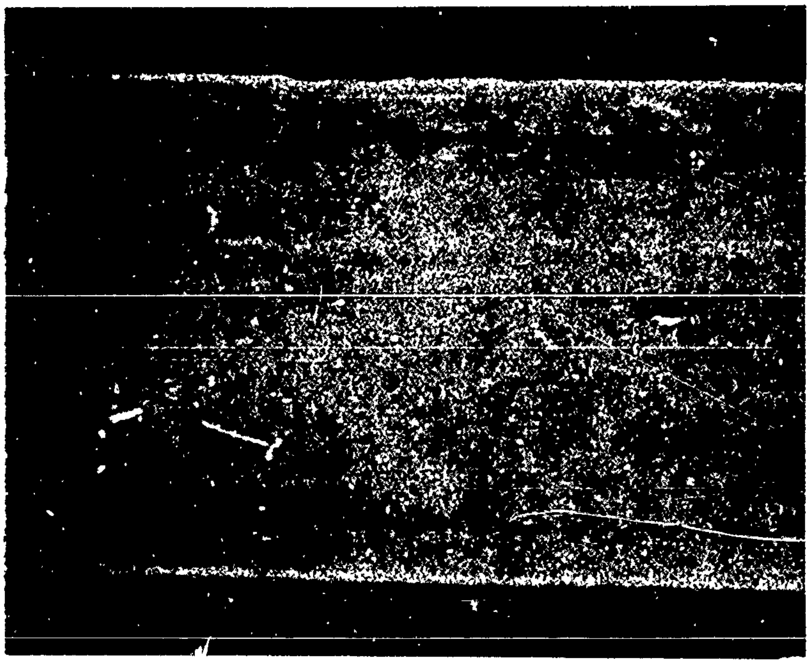

Figure 18. Specimen No. 128 Tensile Tested at 1300 F in Water Vapor/Hydrogen Environment With a Mixture Ratio of 1.00; Not Etched; 100X

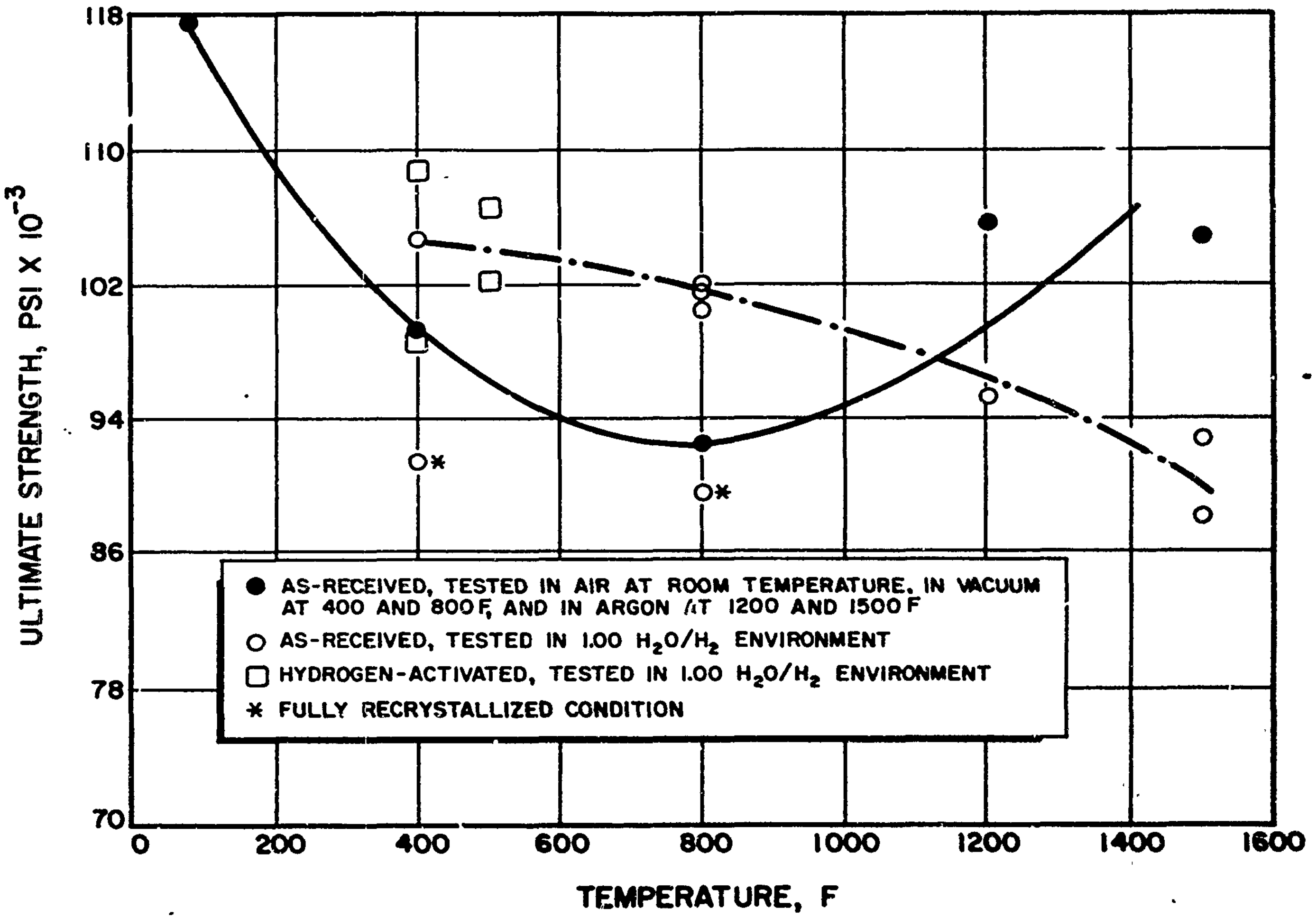

Figure 19. Ultimate Strength of B-66 Columbium Alloy as a Function of Temperature in $H_2O/H_2$ Environments With a Mixture Ratio of 1.00

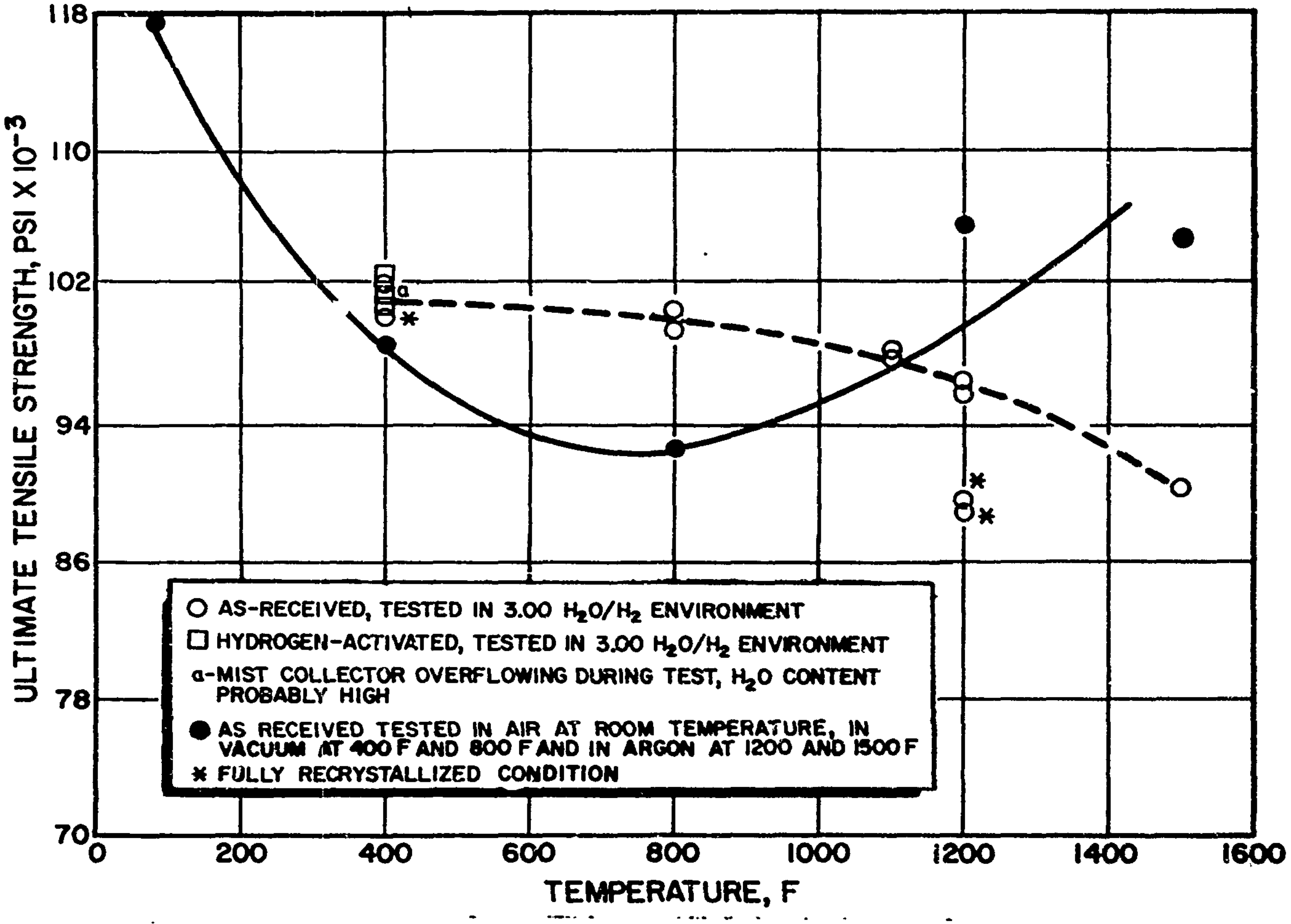

Figure 20. Ultimate Strength of B-66 Columbium Alloy as a Function of Temperature in $H_2O/H_2$ Environments With a Mixture Ratio of 3.00

during these tests. The fully recrystallized specimens had lower strength than did the partially recrystallized specimens.

The amount of oxygen and hydrogen absorbed during the tests on B-66 alloy at temperatures between 400 and 1200 F in both $H_2O/H_2$ environments is very low compared to that absorbed by columbium. Between 1100 F and 1500 F, the amount of oxygen and hydrogen absorbed increased with increasing temperature, and at 1500 F, the amount absorbed is somewhat more in B-66 than it is in columbium. The oxygen and hydrogen contents that were absorbed were slightly higher for the tests at 400, 800, and 1500 F in the 1 $H_2O/H_2$ environment than for the tests in the 3 $H_2O/H_2$ environment. However, at 1200 F, the amount of oxygen and hydrogen absorbed was greater in the 3 $H_2O/H_2$ environment than in the 1 $H_2O/H_2$ environment.

The hydrogen analyses of the B-66 specimens indicate that the ratio of oxygen absorption to hydrogen absorption during the tests was between 8 and 9 for specimens tested in the 3 $H_2O/H_2$ environment at 800 to 1500 F and in the 1 $H_2O/H_2$ environment at 1200 and 1500 F. The fact that these ratios are so close to the theoretical ratio of 8 would indicate that substantially all of the hydrogen absorption resulted from reaction with water vapor and not from direct absorption from the hydrogen in the gas mixture. The ratio of oxygen absorbed to hydrogen absorbed for specimens tested at 800 F in the 1 $H_2O/H_2$ environment was less than 8 indicating absorption of hydrogen from the hydrogen gas. The oxygen and hydrogen absorption that occurred during the 400 F tests in both $H_2O/H_2$ environments was low and rather erratic. In general, there was fairly good agreement between the oxygen and hydrogen absorption as determined by chemical analyses and as determined by weight change during the tests. This agreement would indicate that the oxide removal during sampling was not appreciable.

It is of interest to note that the equilibrium hydrogen concentration in B-66 alloy in contact with hydrogen at 1500 F is 430 ppm, as measured at Rocketdyne. From the data obtained by Albrecht (Ref. 7) on columbium, the equilibrium hydrogen concentration in contact with hydrogen at 1/2 and 1/4 atmosphere pressure in B-66 alloy would be reduced to approximately 310 and 200 ppm. These estimations were made on the basis that the reduction of hydrogen solubility with decreasing pressure is proportionately the same for columbium and B-66 alloy. Therefore, the hydrogen concentration in the B-66 specimens tested at 1500 F is higher than the predicted equilibrium hydrogen content of a specimen in contact with hydrogen gas at these pressures (the partial pressure of the hydrogen in the 1 and 3 $H_2O/H_2$ environments). Furthermore, the hydrogen could not have evolved on cooling from 1500 F in the flowing argon atmosphere following the tensile test although Walter and Offner (Ref. 6) have shown that hydrogen evolution from columbium in flowing argon occurs at temperatures above 900 F. This lack of evolution was probably the result of an oxide surface layer.

# SUMMARY AND CONCLUSIONS FOR COLUMBIUM AND B-66 ALLOY IN VARIOUS ENVIRONMENTS

For ease of comparison, both the strength and ductility curves of columbium are plotted in Fig. 21. In a similar manner, the curves of the B-66 columbium alloy are presented in Fig. 22.

The tensile tests on columbium indicate ductility minimums at 400 and 1050 F. However, the ductility at 400 F was only slightly less in the $H_2O/H_2$ atmospheres than it was in argon. The ductility minimum at 1050 F appears to be associated with hydrogen since a hydride phase was found in these specimens after testing. Between 1050 and 1500 F there is also some decrease in ductility, and above 1050 F embrittlement decreases with increasing $H_2O/H_2$ ratio. Only at 1050 F was there a considerable reduction of ductility compared to tests in an inert environment. And, even at 1050 F, there was still approximately 20-percent elongation after the 50- to 60-minute exposure to the $H_2O/H_2$ atmosphere.

The most interesting result of these tests is the relative stability of columbium in $H_2O$ environments. Columbium is virtually unstable in air over nearly the entire temperature range of these tests, yet these specimens withstood 50- to 60-minute exposures to $H_2O/H_2$ atmospheres under stress without loss of strength and with less than 50-percent reduction of ductility at any of the temperatures tested. Oxygen and hydrogen absorption increased with increasing temperature, but even at 1500 F, the highest temperature tested, the oxide was adherent and present only as a thin surface layer. These results indicate that, at least under certain conditions, columbium could be used without protective coatings in $H_2O/H_2$ environments for exposure times up to 1 hour at temperatures below 1500 F. The effect of increasing the pressure to over 1 atmosphere on the rate of oxidation is not known. However, if the oxidation rate is diffusion and not surface reaction dependent, increasing the pressure would have little effect on the rate of oxidation.

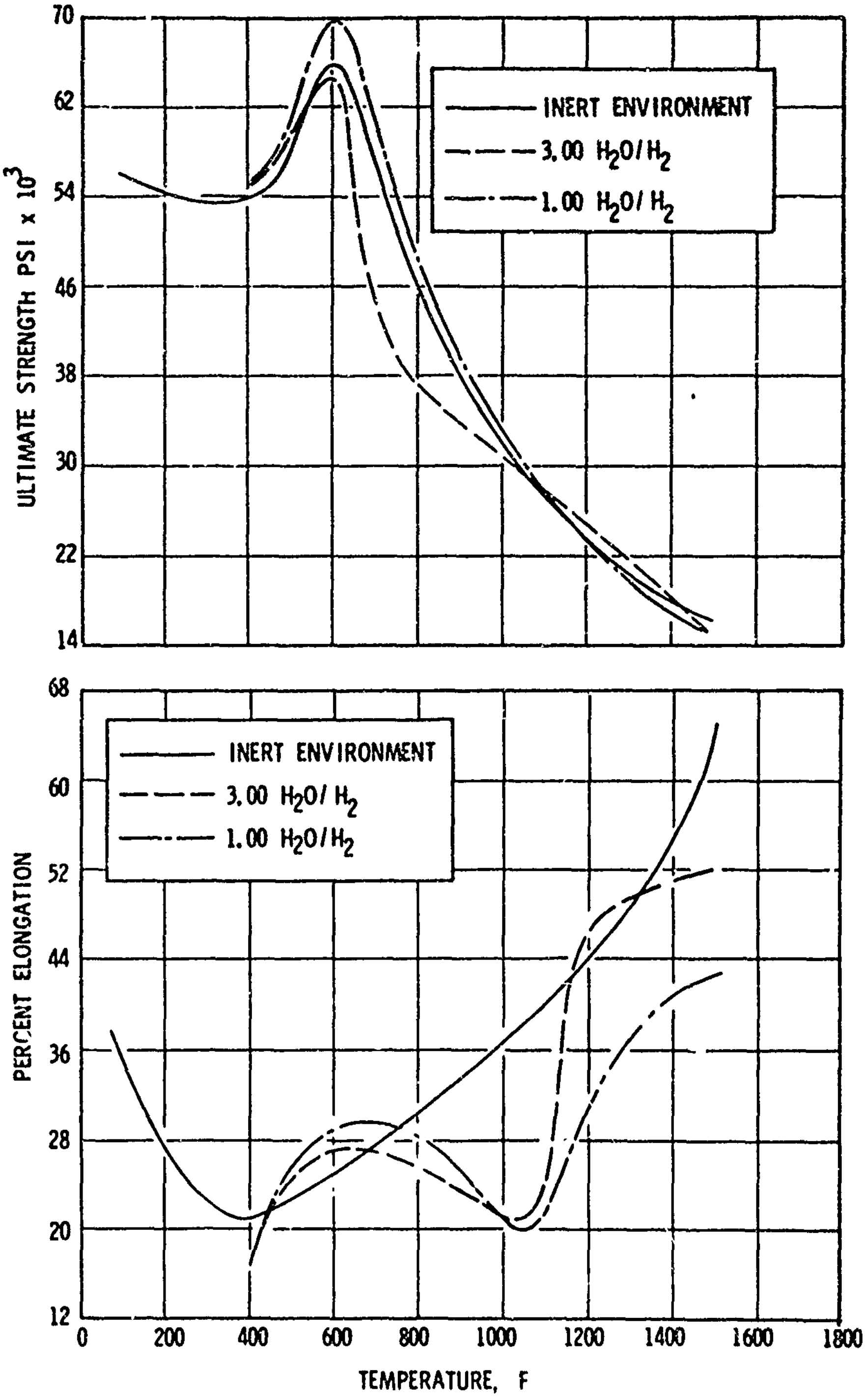

Figure 21. Ultimate Tensile Strength and Ductility of Columbium as a Function of Temperature in Various Environments

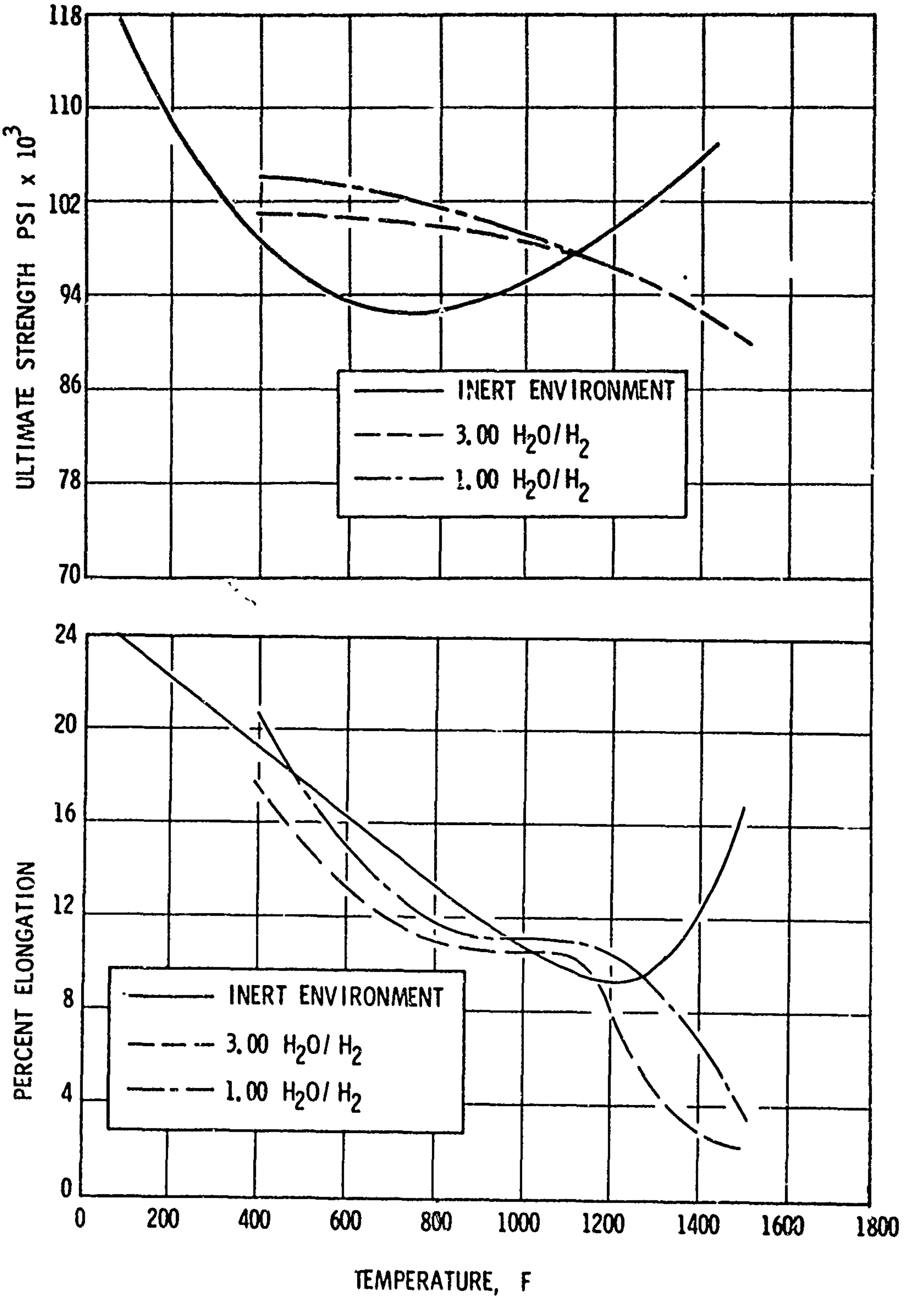

Figure 22. Ultimate Tensile Strength and Ductility of B-66 Columbium Alloy as a Function of Temperature in Various Environments

The surface oxide formed on columbium from reaction with water vapor evidently acts as a barrier to hydrogen absorption as is evidenced by the low hydrogen contents present after testing in the $H_2O/H_2$ environments. Hydrogen absorption appears to be, instead, mainly dependent upon the hydrogen released from reaction with water vapor. Evidently, the atomic hydrogen that is released on oxidation can more readily penetrate the oxide than molecular hydrogen which must dissociate to atomic hydrogen after adsorption onto the surface before it can be absorbed into the metal. The evidence in favor of this mechanism of hydrogen absorption in columbium by reaction with water is, however, not as strong as it is in the B-66 alloy. It is, thus, quite possible that embrittlement of columbium at 1050 F is caused, at least in part, from hydrogen absorbed from the gaseous hydrogen phase. If this were true, then increasing the hydrogen pressure by increasing the $(H_2O/H_2)$ pressure would effect a further decrease of ductility at this temperature. This is because the rate of hydrogen diffusion is sufficiently fast at 1050 F so that hydrogen absorption would be pressure dependent. The results of the mechanical tests on columbium in high-pressure hydrogen will show the degree of embrittlement which can be effected by exposure to hydrogen at high pressures. This information will be useful in predicting, at least to some degree, the expected compatibility of columbium with $H_2O/H_2$ environments at high pressures. However, the importance of testing in high-pressure $H_2O/H_2$ environments cannot be overestimated for proving the compatibility of any material to be used in these atmospheres.

The $H_2O/H_2$ environments effected a slight reduction of ductility at 800 F and considerable embrittlement at 1500 F in B-66 alloy. If the B-66 specimens were previously hydrogen activated and then tested in the 1 $H_2O/H_2$ atmosphere, a reduction of ductility also occurred at 400 F. Embrittlement of the hydrogen activated specimens is dependent upon the hydrogen partial pressure. This is evidenced by the fact that embrittlement of the activated specimens was much more severe when tested in pure hydrogen, and, also, no embrittlement occurred when the activated specimens were tested in the 3 $H_2O/H_2$ environment. The susceptibility of B-66 alloy to embrittlement at low temperatures in the hydrogen-activated condition may not be particularly pertinent to service conditions involving exposure only to $H_2O/H_2$ environments. This is because hydrogen absorption into B-66 alloy from $H_2O/H_2$ environments is evidently associated only with the hydrogen released on reaction with water vapor and the amount of hydrogen absorbed is probably too low to result in activation.

Absorption of oxygen and hydrogen was considerably less in B-66 alloy than in columbium except at 400 and 1500 F. At 400 F interstitial absorption was very low for both materials; at 1500 F interstitial absorption was approximately the same for both materials. The ratio of oxygen absorbed to hydrogen absorbed was close to 8 for tests performed on B-66 alloy between 800 and 1500 F which indicates that hydrogen absorption occurred primarily from the hydrogen released during oxidation by water vapor. The oxide phase on B-66 alloy is evidently a barrier to hydrogen penetration from the gas phase, although this oxide does not prevent hydrogen penetration by the nascent hydrogen released on reaction with water vapor.

The low interstitial absorption which occurred at 400 F for both materials would suggest that embrittlement at this temperature occurs by a surface-type reaction. The mechanism may involve lowering of the surface energy of a newly formed crack by chemical adsorption of hydrogen onto the crack surface.

The decrease in ductility of the B-66 alloy tested at 1500 F in both $H_2O/H_2$ environments is associated with a relatively thick oxide layer. The oxide formed on B-66 alloy by reaction with oxygen is evidently not as protective as is the oxide which forms on exposure of columbium to water vapor at elevated temperatures. The higher water content of the 3 $H_2O/H_2$ environment effected increased embrittlement in all but the hydrogen activated specimens compared to testing in the 1 $H_2O/H_2$ environment. Therefore, the results indicate that embrittlement of B-66 alloy in the $H_2O/H_2$ atmospheres is caused by oxidation and the use of B-66 alloy at 1500 F in either of the $H_2O/H_2$ environments may require an oxidation protection coating. However, oxidation protection coatings may prevent oxidation, but allow the penetration of hydrogen from the hydrogen gas. Thermal cycling of coated specimens may, therefore, effect hydrogen activation and embrittlement at low temperatures.

As with columbium, the $H_2O/H_2$ environments also did not affect the mechanical strength of B-66.

# FUTURE EFFORT

It is anticipated that the impetus toward the utilization of refractory alloys in regeneratively cooled rocket and ramjet engines, so vital to the nation's military and space objectives, will increase significantly during the next few years. The initial steps to improve the performance of these engines will result in materials requirements, particularly in the thrust chamber, which reasonably can be met only with the refractory alloys. Thus, a refractory alloy technology that will allow the use of these alloys with confidence in regeneratively cooled rocket or ramjet engines must be developed as rapidly as is feasible.

As noted in the introduction, three areas require investigation for the successful application of columbium and tantalum alloys in nozzles of advanced, high-performance engines that have hydrogen or water vapor/hydrogen exhaust gases. The three areas are: (1) the effect of hydrogen at high pressures and elevated temperatures on mechanical properties, (2) the solubility and rates of absorption and desorption of hydrogen at high temperatures and high hydrogen pressures, and (3) the effect of water vapor/hydrogen environments on mechanical properties.

This report contains the results of a study of the effect of water vapor/hydrogen environments on the mechanical properties of columbium and the B-66 columbium alloy. A similar program should be conducted on tantalum and a tantalum alloy, e.g., Ta-10W.

Investigations of areas (1) and (2) above should be conducted on columbium, the B-66 columbium alloy, tantalum, and Ta-10W. Rocketdyne has set up equipment and facilities for investigations in both of these areas. For the determination of mechanical properties in high-pressure hydrogen at elevated temperatures, an apparatus was designed in a joint effort with Ring Engineering, Reseda, California, and was built by Ring Engineering for Rocketdyne. With this apparatus, tensile tests can be conducted in high-pressure hydrogen at elevated temperatures. The apparatus is designed to operate at gas pressures up to 5000 psig and at temperatures up to 2500 F. However, at this time, the hydrogen supply and control system is limited to a 1500-psig operation, but modification to a 5000-psig operation would not be difficult. Also, equipment has been set up at Rocketdyne for the determination of solubility and rates of absorption and desorption of hydrogen at hydrogen pressures up to 1500 psig and at temperatures up to 1800 F.

The results of these initial programs will suggest others, but some can be anticipated. Coatings may be required to protect columbium and tantalum alloys from oxidation and/or hydrogen absorption in hydrogen and water vapor/hydrogen atmospheres. Such coatings would have to be tested in these atmospheres at high pressures. A number of factors determine the susceptibility of metals to hydrogen embrittlement, and many of these factors are a function of alloy content. Therefore, through alloying, the effect of hydrogen on the properties of columbium and tantalum can at least be decreased and thereby reduce the demands placed on the hydrogen barrier coatings. Results of qualitative studies at Rocketdyne indicate that thermal diffusion of hydrogen from high-temperature to low-temperature regions, where the effect of the hydrogen is more severe, may be a serious problem and will require quantitative studies. Clarification of the mechanisms of hydrogen embrittlement of columbium and tantalum would aid in indicating methods of reducing the embrittling effects of hydrogen.

In addition to the studies on columbium- and tantalum-base alloys, the behavior of molybdenum- and tungsten-base alloys in $H_2O/H_2$ environments requires investigation.

# REFERENCES

1. Walter, R. J.: The Columbium-Hydrogen System and Hydrogen Embrittlement of Columbium, Research Report 64-6, Rocketdyne, a Division of North American Aviation, Inc., Canoga Park, California, February 1964.
2. Battles, J. E. et al.: "Research on the Oxidation Behavior of Tungsten," ARL 62-324, April 1962.
3. Lysyj, I.: "Apparatus for the Determination of Water Para Isomer Ratio and the Detection Impurities in Cryogenic Samples of Hydrogen," ISA Proceedings, 1963.
4. Walter, R. J. and W. T. Chandler: "Compatibility of Tantalum and Columbium Alloys with Hydrogen," AIAA Journal, Vol. 4, No. 2, 1966, 302-307.
5. Walter, R. J. and W. T. Chandler, "Columbium-Hydrogen Constitution Diagram," Trans. of Met. Soc. of AIME, Vol. 233, April 1965, 762-765.
6. Walter, R. J. and H. G. Offner: "Determination of Hydrogen in Niobium," Analytical Chemistry, Vol. 36, August 1964, 1779-1781.
7. Albrecht, W. M., W. D. Goode, and M. W. Mallett: "Reactions in the Niobium-Hydrogen System," Journal of the Electrochemical Society, Vol. 106, November 1959, 981-986.

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13 ABSTRACT

The results of an experimental investigation of the effect of water vapor/hydrogen environments on the mechanical properties of columbium and the B-66 columbium alloy are presented. Tensile tests were conducted on specimens of these materials in water vapor/hydrogen environments with $H_2O/H_2$ mixture ratios of 1 and 3.

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