

AD 607274

APL TDR 64-116
Part I

MATERIALS INVESTIGATION, SNAP 50/SPUR PROGRAM
PART I. Creep-Rupture Properties of Stress-Relieved TZM Alloy

TECHNICAL DOCUMENTARY REPORT NO. APL-TDR-64-116, PART I
OCTOBER, 1964

COPY	OF	1/1
HARD COPY	\$.	
MICROFORME	\$.	

AF Aero Propulsion Laboratory
Research and Technology Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

BPSN: 3(6399-675A)

[Prepared under Contract No. AF33(657)-10922
by The Garrett Corporation,
Air Research Manufacturing Division, Phoenix, Arizona;
R. L. Salley and E. A. Kovacevich, Authors]

FOREWORD

This report was prepared by the AiResearch Manufacturing Company of Arizona, a division of The Garrett Corporation, Phoenix, Arizona. The activities discussed in this report were conducted under United States Air Force Contract AF33(657)-10922 [BPSN: 3(6399-675A)]. The contract was administered by the Flight Vehicle Power Division, AF Aero Propulsion Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. Mr. C. H. Armbruster was the Project Engineer for the Laboratory, and Mr. J. H. Dannan directed the SPUR engineering program at AiResearch.

This report covers activities conducted from June 1963 to April 1964 on the "Creep-Rupture Properties of Stress-Relieved TZM Alloy" and is one of five materials evaluation tasks performed by the Battelle Memorial Institute under the general supervision of AiResearch.

Acknowledgment is given to Dr. E. M. Simons, who directed the work at the Battelle Memorial Institute; Messrs. R. L. Salley and E. A. Kovacevich, who supervised the activities for AiResearch; and Mr. L. D. Six, Chief of the Advanced Power Systems Project at AiResearch.

This report is assigned supplementary report number APS-5092-R by AiResearch.

ABSTRACT

The results of experimental investigations to determine the effect of potassium on the creep-rupture properties of the TZM alloy are presented herein. The tests were conducted at 1800° and 2000°F, with and without exposure to saturated potassium vapor. The results indicated that the creep-rupture behavior was not influenced significantly by exposure to potassium vapor for periods of approximately 1,000 hours. However, some mass-transfer type corrosion was observed. This signifies that it is dangerous to extrapolate the results of this study to 10,000 hours, because progressive mass transfer might eventually cause accelerated creep and premature failure.

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

TABLE OF CONTENTS

	<u>Page</u>
I INTRODUCTION AND OBJECTIVE	1
II TEST MATERIALS AND SPECIMEN PREPARATION	2
III TEST APPARATUS	7
IV TEST PROCEDURE	10
V TEST RESULTS	13
A. Effect of Internal Pressure	13
B. Thermocouple Diffusion Reaction	13
C. Crystal Deposits	22
D. Corrosion Effects	27
E. Creep-Rupture Behavior	27
VI CONCLUSIONS	29
VII REFERENCES	30

ILLUSTRATIONS

FIGURE		PAGE
1	TZM Creep-Rupture Specimen and End Plug	3
2	Potassium Hot-Gettering Loop	5
3	Schematic Arrangement of Conventional Test Apparatus Utilized for Determining Effect of Potassium Vapor on Creep of TZM Alloy	8
4	Portion of Vacuum-Creep-Test Laboratory	9
5	Specimen and Pull Bars Partially Assembled; Below, Ruptured TZM Specimen	11
6	Deformation-Time Curves for Stress-Relieved TZM Alloy at 1800°F	15
7	Deformation-Time Curves for Stress-Relieved TZM Alloy for 2000°F with and without Potassium Vapor Environment	16
8	Stress versus Minimum Creep Rate for Stress-Relieved TZM Alloy at 1800°F and 2000°F	17
9	Design Curves for Stress-Relieved TZM Alloy at 1800°F	18
10	Design Curves for Stress-Relieved TZM Alloy at 2000°F	19
11	Longitudinal Sections through Zones where Chromel-Alumel Thermocouple Beads Reacted with TZM in Specimen 7	21
12	Crystal Deposits found on ID Surface of Specimen 5, which Ruptured after 641.3 Hours at 2000°F under 45,000-psi Stress	23
13	Crystal Deposits and Etched Band on ID Surface of Specimen 2 from Test 11, which ran 1539 Hours at 1800°F under 64,000-psi Stress	24
14	Comparison of Pre- and Post-Test Microstructures of Stress-Relieved TZM Alloy	28

SECTION I - INTRODUCTION AND OBJECTIVE

The candidate material selected for fabrication of the wheel and blade components for the potassium-vapor turbine in the SPUR power plant is the TZM alloy (Mo - 0.5 w/o Ti - 0.08 w/o Zr). This material appears to have the necessary fabricability, strength, and resistance to corrosion by potassium. Another important property for this application is resistance to creep, since excessive creep of the turbine blades under the centrifugal stresses imposed can cause rotor unbalance and rubbing of the blade tips on the shroud.

The turbine can be designed on the basis of vacuum-creep data at the temperatures of interest, provided that exposure to potassium vapor does not cause accelerated creep. The objective of this study was to compare the creep-rupture behavior of the TZM alloy in a vacuum or inert atmosphere with its creep-rupture behavior in saturated potassium vapor at 1800° and 2000°F.

To circumvent the temperature-instability problems associated with 2000°F boiling-refluxing potassium in a bellows-sealed chamber, hollow creep-rupture specimens were used. For the potassium-vapor exposures, a small amount of potassium was sealed into each specimen cavity and the tests were run in conventional vacuum-creep equipment. Control tests (vacuum or helium in the specimen cavity) utilized the same specimen design, but without potassium.

SECTION II - TEST MATERIALS AND SPECIMEN PREPARATION

The TZM specimen stock was procured from the Universal Cyclops Steel Corporation in the form of 3/4-inch-diameter, arc-vacuum-cast, hot-rolled, stress-relieved (1 hour at 2200°F) ground bar. The vendor's analysis showed the following constituents (weight percent):

Ti	0.50	Cr	<0.001	Fe	0.0015
Zr	0.09	W	0.006	O	0.0018
C	0.027	Sn	0.001	N	0.0001
Si	0.0035	Ni	0.002	H	0.0003
Al	<0.001	Pb	<0.001		

This material was from Mill Order No. RW9-1984-G, Heat No. KD-TZM-1155B. The room-temperature mechanical properties (longitudinal direction) of two samples tested by the vendor were as follows:

Hardness	295 and 300 VHN
Yield point	112.6 and 113.8 kpsi
Ultimate tensile strength	130.9 and 129.7 kpsi
Elongation	21.6 and 24.5 percent
Reduction in area	40.1 and 51.3 percent

Specimens were fabricated from this material according to the drawing shown in Figure 1, using the following procedure:

- (1) Bar stock was sawed into 3-9/16-inch lengths.
- (2) The 1/2-inch hole was gun-bored and honed to a surface finish of <10 μ in. rms.
- (3) Using a lathe with a collet on one end and a live center at the other, the OD's were turned to size and threaded, leaving 5 to 15 mils of excess stock on the gauge sections for finish grinding.
- (4) The gauge lengths and fillets were finish ground in a spindle grinder to a surface finish of <10 μ in. rms.
- (5) All specimens were then measured for internal and external surface roughness, internal and external diameters, and gauge length.

Special-purity potassium, obtained from MSA Research Corporation, was used. A certified analysis of this material, supplied by the vendor, was as follows:

<u>Element PPM</u>	<u>Element PPM</u>	<u>Element PPM</u>
Na 30	Cu 9	Be < 1
Fe 35	Pb < 5	Ag < 1
B <10	Cr < 5	Zr <10
Co < 5	Si <25	Sr < 1
Mn 5	Ti < 5	Ba < 1
Al 6	Ni 12	Ca 10
Mg 4	Mo < 3	O 10
Sn < 5	V < 1	

Although the purity of this potassium was more than adequate for charging the creep-rupture specimens, it was subjected to a hot-gettering step in order to minimize contamination during the transfer and specimen-charging operations. Figure 2 illustrates the hot-gettering loop. Potassium from the shipping container (fill tank) was melted and transferred by gas pressure to the gettering pot. The liquid was then circulated through the loop at 1200°F for at least 24 hours. The gettering foil was a Zr - 30 w/o Ti alloy, 5 mils thick. All valves were of the sealed, bellows type.

After the gettering period, the potassium was frozen in the transfer vessel; this vessel was then removed from the loop at the two flanges in the horizontal legs and transferred to a glove box. The glove box was evacuated and backfilled with pure helium. One end of the transfer vessel was then fitted with an orifice plate and the other with a screw-operated plunger.

The creep-rupture specimens, with one end plug Heliarc-welded in place and leak-checked, were charged with potassium inside the glove box as follows. A solid potassium rod about 3 inches long was extruded mechanically from the transfer vessel, cut off with a Teflon-coated razor blade, and discarded. Several cubic centimeters of potassium were then extruded into a glass jar on a hot plate. The jar had been washed with a detergent, rinsed with acetone, and dried with alcohol. A similarly cleaned hypodermic needle was then used to extract and insert 1/4 cu cm of molten potassium into each specimen cavity. The second end plug was then welded into each specimen, and the specimens were removed from the glove box and given a final leak check with the mass-spectrograph helium leak detector.

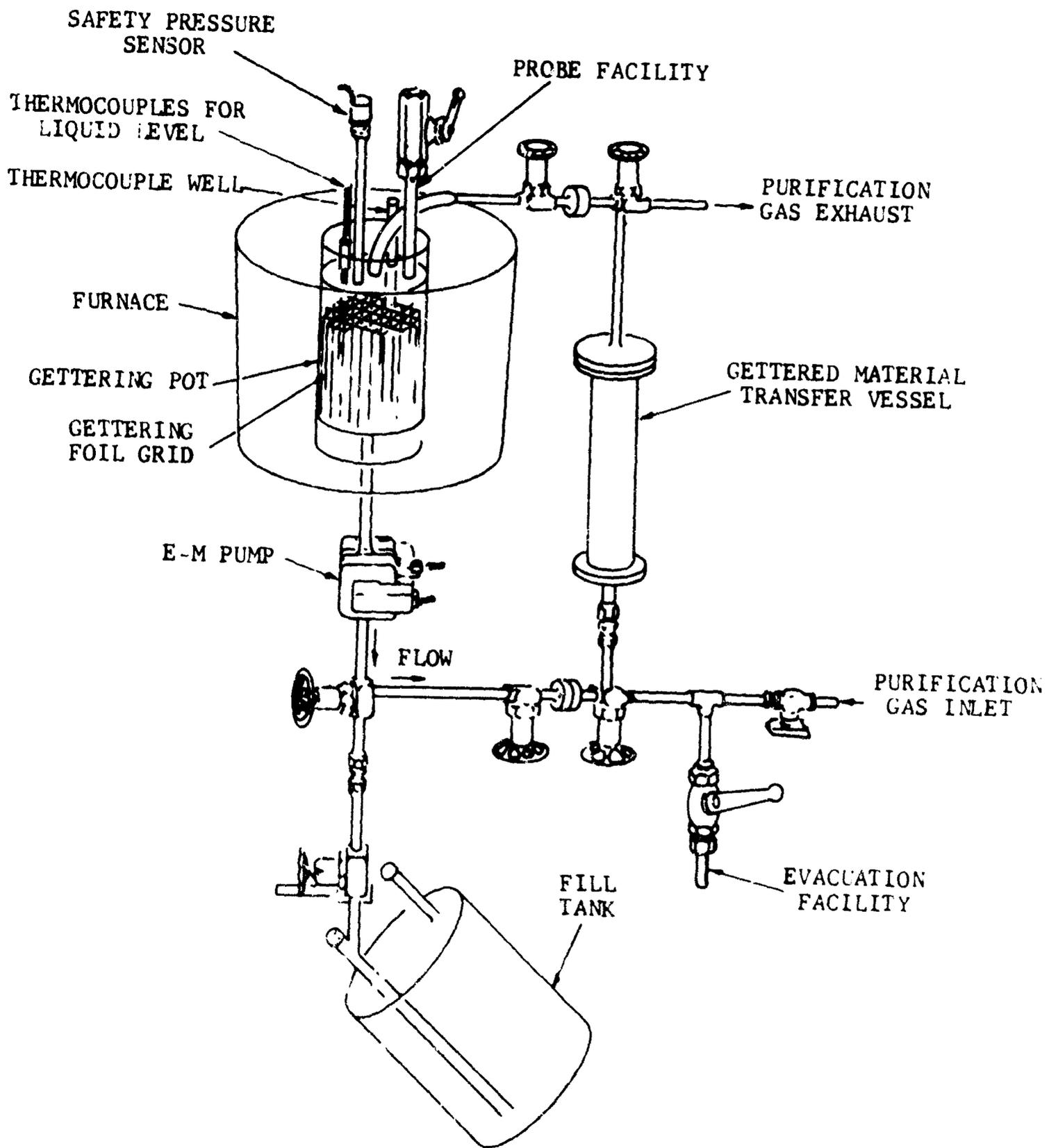


FIGURE 2. POTASSIUM HOT-GETTERING LOOP

At the same time that the specimens were being charged, samples were taken for oxygen determinations. One sample, extruded directly into the mercury amalgamation apparatus, showed 14.5 ppm oxygen. Three others showed 38, 63, and 67 ppm oxygen, respectively. The higher values were obtained with samples that had been allowed to stand for appreciable periods of time in Tygon-sealed glass tubes outside the glove box before the tubes were flamed off and inserted into the amalgamation apparatus. Since these samples tarnished visibly during storage, it was concluded that they were contaminated after they were removed from the glove box. Consequently, it is felt that although three samples were higher than 15 ppm (38, 63, and 67 ppm) oxygen, the analysis of the first sample (14.5 ppm) represents an accurate oxide concentration in the potassium employed in these tests.

SECTION III - TEST APPARATUS

The apparatus utilized for conducting the creep-rupture experiments on the TZM alloy is shown schematically in Figure 3. Figure 4 shows a portion of the vacuum-creep-test laboratory at Battelle, illustrating the creep frames, lever system, mechanical and diffusion pumps, and method of making optical strain measurements.

The specimens were stressed by placing dead weights on a hanger attached to the rear of the load lever. The mechanical advantage was approximately 9:1, varying slightly from unit to unit. Each unit was equipped with an electric timer, which started when the load was applied and stopped automatically when the specimen ruptured. In routine operation during most tests, the vacuum system maintained a chamber pressure that was well below the bottom of the scale (10^{-3} torr) on a thermocouple-gauge indicator. Some of the newer units were equipped with ionization gauges, normally indicating 5×10^{-5} to 5×10^{-4} torr during a test.

The furnace resistance windings were Hoskins 875 alloy for the 1800°F runs and molybdenum for the 2000°F runs. The windings were tapped at nine axial locations to permit short sections at hot zones to be shunted out, thus maintaining a uniform axial temperature in the specimen. A thermocouple-actuated Foxboro controller regulated the specimen temperature at the desired value within about 5 degrees at 2000°F .

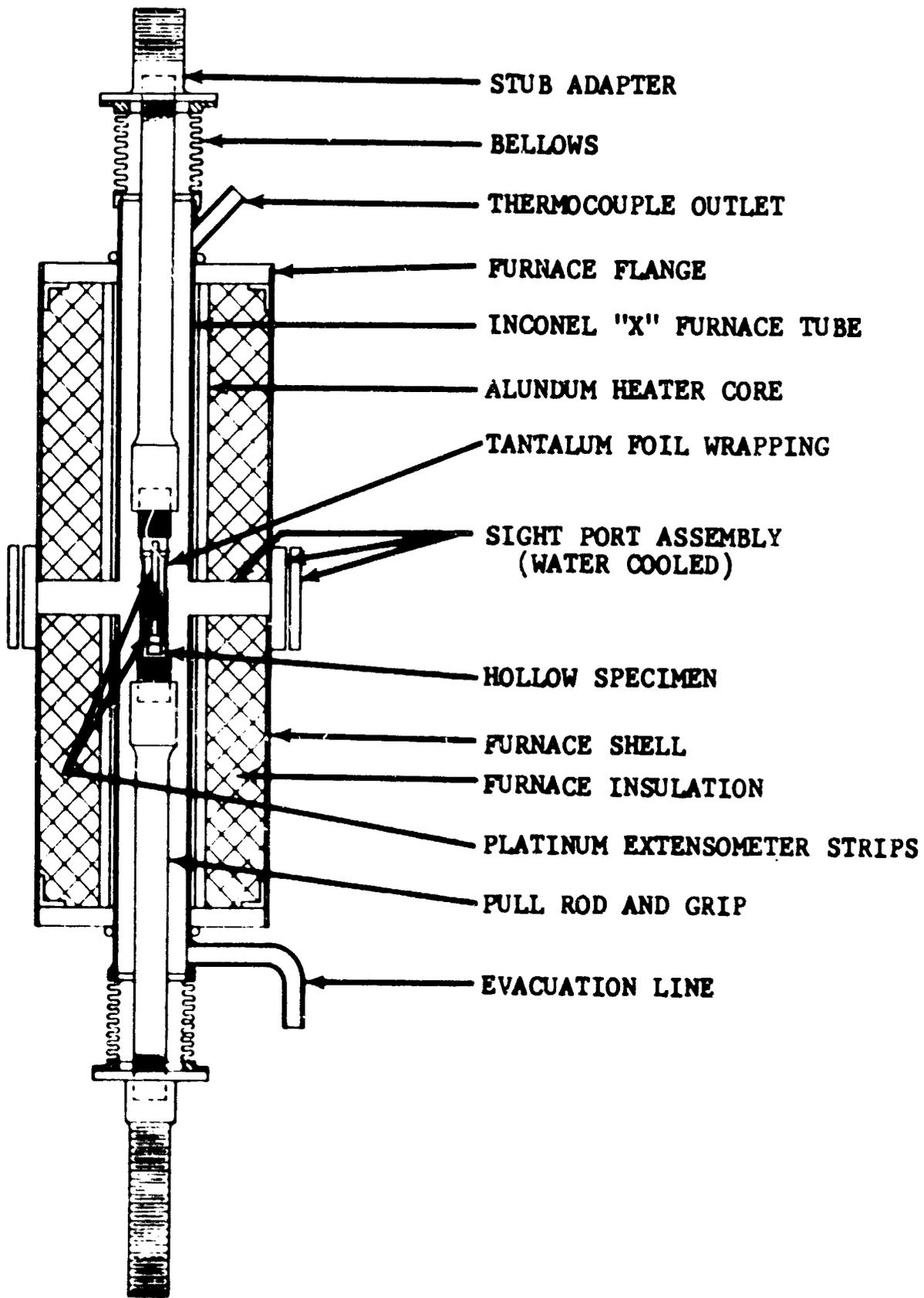


FIGURE 3. SCHEMATIC ARRANGEMENT OF CONVENTIONAL TEST APPARATUS UTILIZED FOR DETERMINING EFFECT OF POTASSIUM VAPOR ON CREEP OF TZM ALLOY

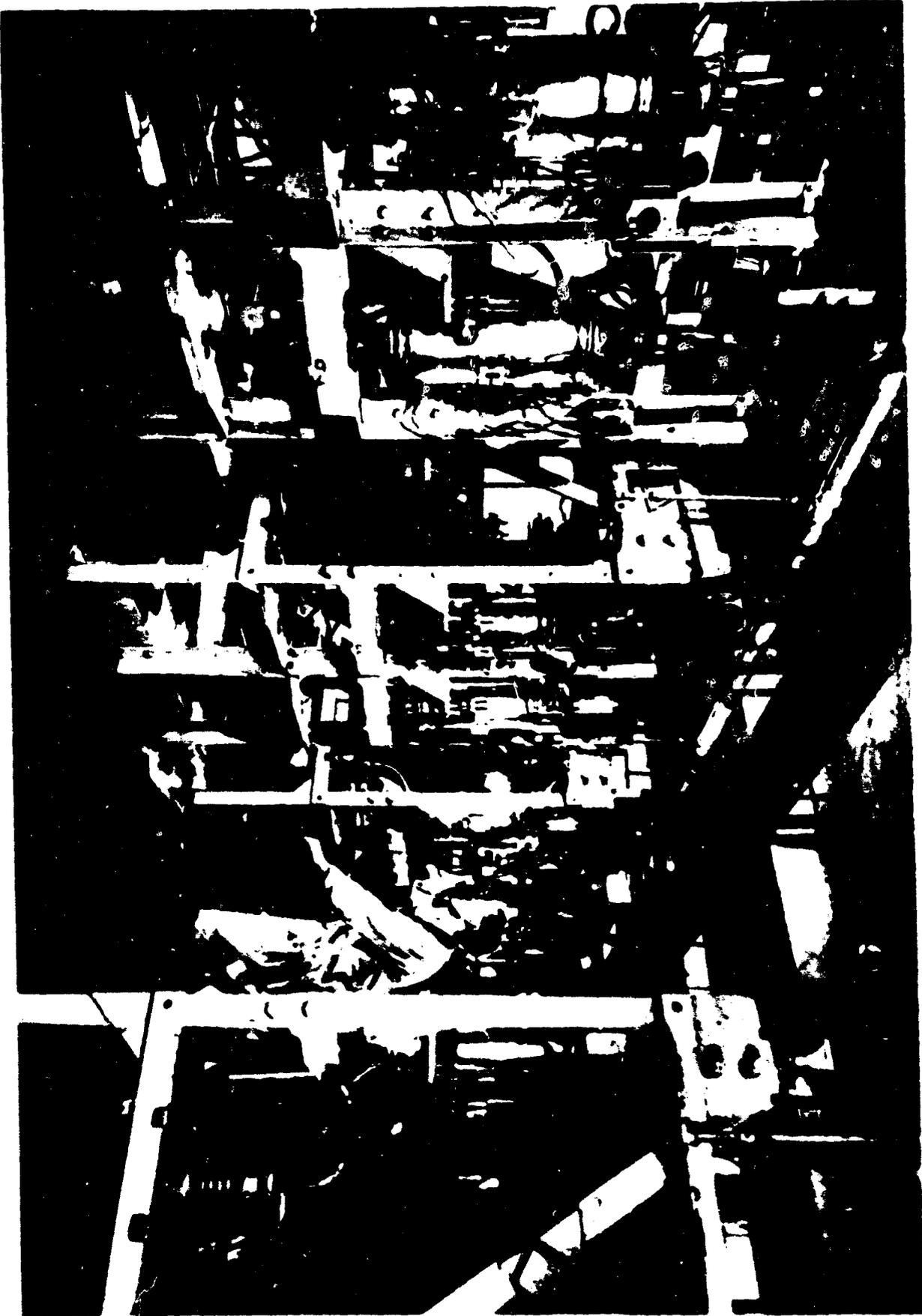


FIGURE 4. PORTION OF VACUUM-CREEP-TEST LABORATORY

SECTION IV - TEST PROCEDURE

The following steps were used in preparing and running a creep-rupture experiment:

- (1) The upper and lower pull rods (which were fabricated from stress-relieved TZM bar stock) were threaded onto the specimen ends.
- (2) The gauge section of the specimen was wrapped with two strips of 1-mil-thick tantalum foil, overlapping about an inch in the center. The wrapping, secured with molybdenum wires, can be seen in the partial assembly in Figure 5. The tantalum foil served to getter traces of reactive gases in the vacuum chamber, thereby reducing contamination of the specimen surface during a test.
- (3) Three Chromel-Alumel thermocouples were wired to the specimen--one in the middle and one near each end of the gauge length--with the beads tight against the tantalum, as shown in Figure 5. In test, the center thermocouple was attached to a Foxboro controller which regulated the current to the furnace. The other two thermocouples were periodically monitored to insure axial temperature uniformity.
- (4) Overlapping platinum extensometer strips were wired at each end of the specimen shoulder, utilizing the circumferential V-grooves (Figure 1) to hold the molybdenum wires in place. One pair of such strips is visible in Figure 5; the other pair is 180 degrees away (behind the specimen). During a test, the separation of the fine reference marks scribed on the sliding platinum strips was measured periodically with a traveling microscope focused through the chamber sight port (Figure 4), which resulted in the direct measurement of strain in the gauge length.
- (5) The ends of the pull bars were fitted with stub adapters, and the whole assembly was inserted in the furnace tube (Figure 3) and sealed to the water-cooled bellows flanges with Neoprene gaskets. The six thermocouple leads were brought out through an insulating elastomeric vacuum seal in the water-cooled thermocouple outlet tube.
- (6) The vacuum chamber was evacuated, and the specimen heated to the desired temperature.

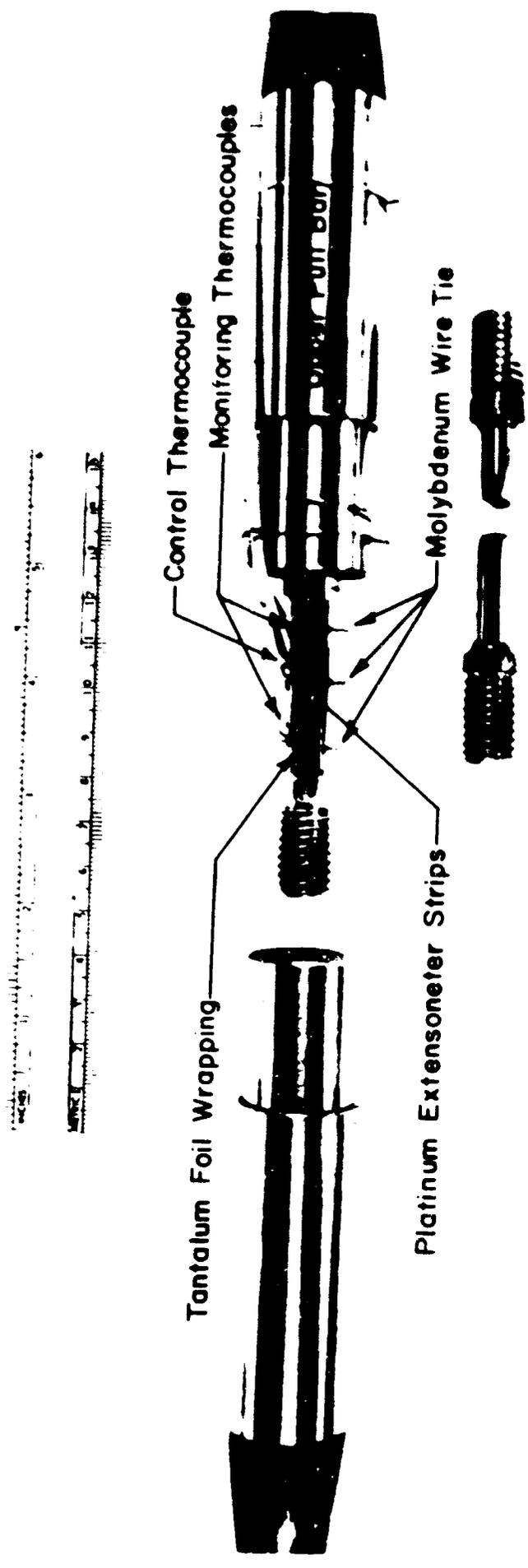


FIGURE 5. SPECIMEN AND PULL BARS PARTIALLY ASSEMBLED;
 BELOW, RUPTURED TZM SPECIMEN

- (7) When equilibrium conditions were achieved (specimen temperature uniform and steady at the desired value), the test was begun by placing predetermined weights on the lever load pan. These weights were calculated to provide the desired axial stress in the specimen, compensating for:
- (a) Pressure difference between the inside and outside of the specimen
 - (b) Pressure difference between the inside and outside of the vacuum chamber
 - (c) Dead weights of loading-system components
 - (d) Lever-arm mechanical advantage
- (8) Strain readings were taken optically at the instant the load was applied, at frequent intervals during the first hour, and then once or twice a day thereafter until the specimen ruptured.

SECTION V . TEST RESULTS

Twelve creep-rupture experiments were conducted during this investigation--seven at 2000°F and five at 1800°F. The test conditions and results are summarized in Table 1 and in Figures 6 through 10.

A. Effect of Internal Pressure

Before adopting a hollow specimen with potassium vapor sealed inside under an atmosphere of helium, the possibility was considered that the multiaxial stresses resulting from the internal pressure due to the helium expansion on heating and to the vapor pressure of the potassium would affect the creep results. At 2000°F, there is an internal pressure of 153 psia from the potassium vapor and about 67 psia from helium expansion, or about 220 psia total internal pressure. The maximum principal stresses induced by this pressure (by Lamé's equations) are 300 psi axial tension, 815 psi tangential tension (at the inner wall), and 220 psi radial compression (at the inner wall). The smallest axial tensile stress used in any of the tests listed in Table 1 was 36,500 psi (Test 7).

It was demonstrated experimentally by Oak Ridge National Laboratory^{1,2} that when the ratio of axial to tangential stresses (σ_z/σ_θ) is greater than 1/2, the axial strain rate is independent of the state of stress and depends only on the stress in the axial direction. Thus, the creep behavior under the triaxial stresses in the current work ($\sigma_z/\sigma_\theta > 40$) would be expected to be indistinguishable from that which would occur under uniaxial tension.

The purpose of Test 2 (solid specimen - no internal pressure) was to get a quick experimental check of this. As can be seen from the very good agreement of the creep curve for Test 2 with those for Tests 1 and 3 in Figure 7, the internal pressure seemed to have no effect on the creep-rupture results. Test 2 also provided confidence that hollow specimens (even without multiaxial-stress considerations) give results comparable to those obtained with solid specimens.

B. Thermocouple Diffusion Reaction

Visual examination of the specimens following the tests revealed isolated spots on the outer surface, varying in size from scarcely visible to about 1/16 inch in diameter and located precisely where the Chromel-Alumel thermocouple beads had been wired to the tantalum-foil wrapping. These reaction zones were most pronounced under the two end thermocouples on specimens which had been at 2000°F for the longest periods of time (Tests 4, 5, and 7). There was generally very little reaction under the center

TABLE 1. STRESS-RUPTURE TEST DATA FOR HOLLOW IZM SPECIMENS
External Atmosphere, Vacuum (<1 μ)

Test No.: Specimen No.:	1	2	3	4	5	6	7	8	9	10	11	12
Internal Atmosphere	Medium	(Solid)	Potassium	Potassium	Potassium	Medium	Vacuum	Potassium	Potassium	Potassium	Potassium	Vacuum
Temperature, °F	2,000	2,000	2,000	2,000	2,000	2,000	2,000	1,800	1,800	1,800	1,800	1,800
Stress, psi	54,000	54,000	54,000	42,500	45,000	45,000	36,500	86,000	86,000	64,000	58,000	64,000
Min Creep Rate, %/hr	0.032	0.062	0.055	0.0041	0.0052	0.012	0.0014	(b)	(b)	0.036	0.00756	0.0145
Total Elongation at Rupture, %	16.4	18.0	14.3	10.0	12.4	13.8	8.8	9.6	14.7	14.7	6.39(a)	10.8
R.A. at Rupture, % (c)	-85	91.5(d)	-85	>85	-85	-85	-85	-85	-85	-85	(a)	85
Time to Reach Indicated Total Elongation, hr												
0.5%	0.2	0.2	0.95	3.0	1.3	0.2	25.7	(b)	--	0.5	1.2	1.1
1.0%	2.3	4.3	3.5	60	38	25	350	(b)	1.4	6.5	47	30.0
2.0%	32	20	17.5	255	235	116	765	(b)	8.7	34.5	225	101.0
3.0%	59	36	36	370	415	190	950	(b)	16	58	600	150.5
Time to Rupture, hr	97.6	80.9	86.6	526.3	641.3	301	1,169	(b)	24.9	108.1	1539(a)	237.4
Appearance of Specimen (e)	D	S.D.	S.D.	S.D.	B	D	B	B	B	B	B	S.D.
Surface Roughness, μin., rms												
OD before test	5-7	4-6	4-7	4-5.5	4-5-6.5	4-6	4-5-5.5	4-6	4-6	4-6	6-9	4-5.5
OD after test	5-6.5	6.5-7.5	4-5-6	8-9	5.5-8	4-5	6-9	6-8	6-3	6-7.5	6-7.5	5-7
ID before test	2.5-3.5	--	5-6.5	4-5-6	5-7	4-6	6-17	4-6	4-6	5-6.5	4-5-4.5	7-9
ID after test	5.5-7	--	14-30	8-17	40-60	7-10	6-8.5	7-9.5	10-15	7-9.5	10-120	17-28

(a) Test terminated prior to rupture.
 (b) Specimen failed on loading.
 (c) Cannot measure accurately on hollow specimen.
 (d) Cross section at break roughly rectangular.
 (e) D = dull; S.D. = slightly dull; B = bright.

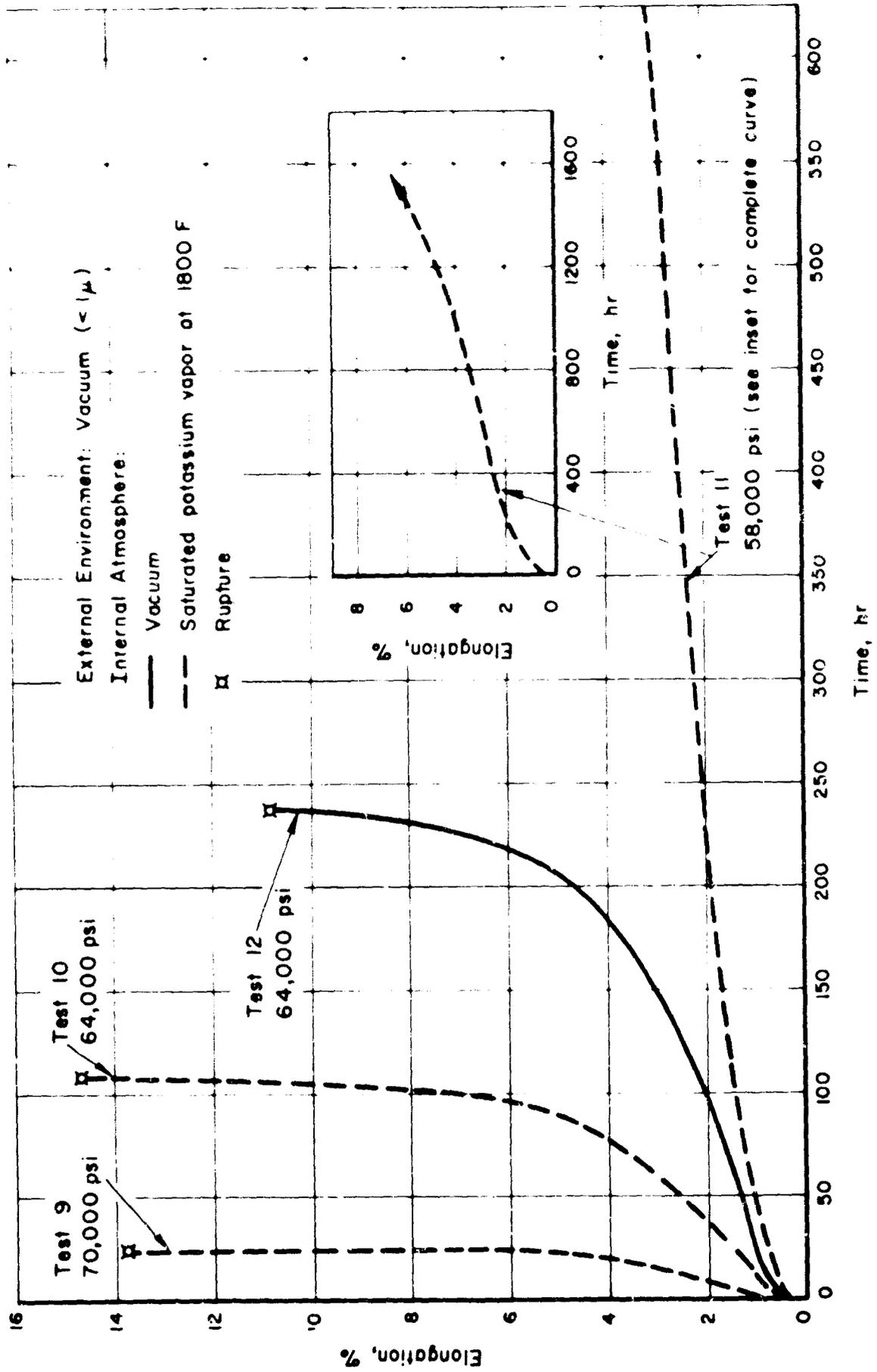


FIGURE 6. DEFORMATION-TIME CURVES FOR STRESS-RELIEVED TZM ALLOY AT 1800 F

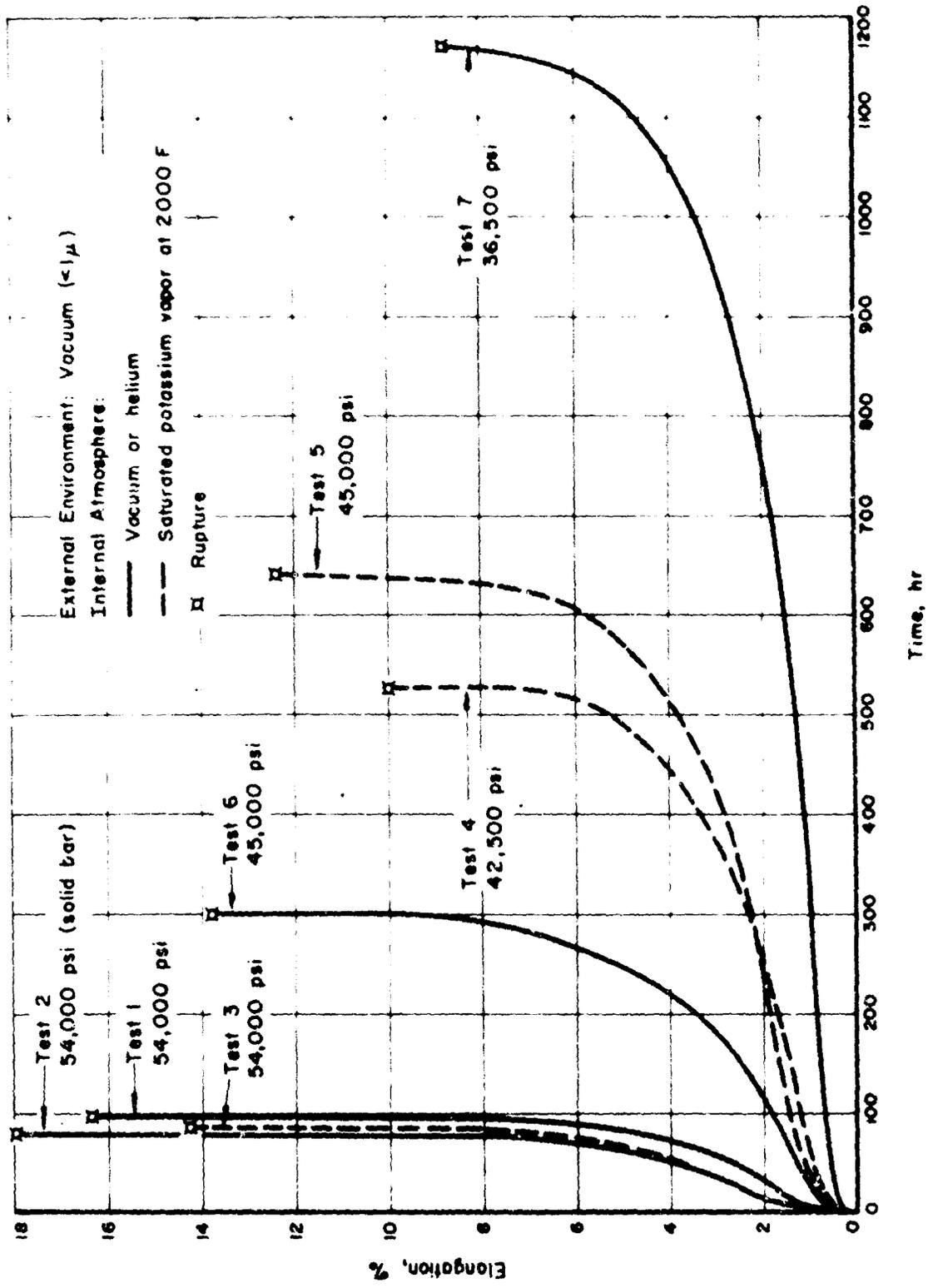


FIGURE 7. DEFORMATION-TIME CURVES FOR STRESS-RELIEVED TZM ALLOY FOR 2000°F WITH AND WITHOUT POTASSIUM-VAPOR ENVIRONMENT

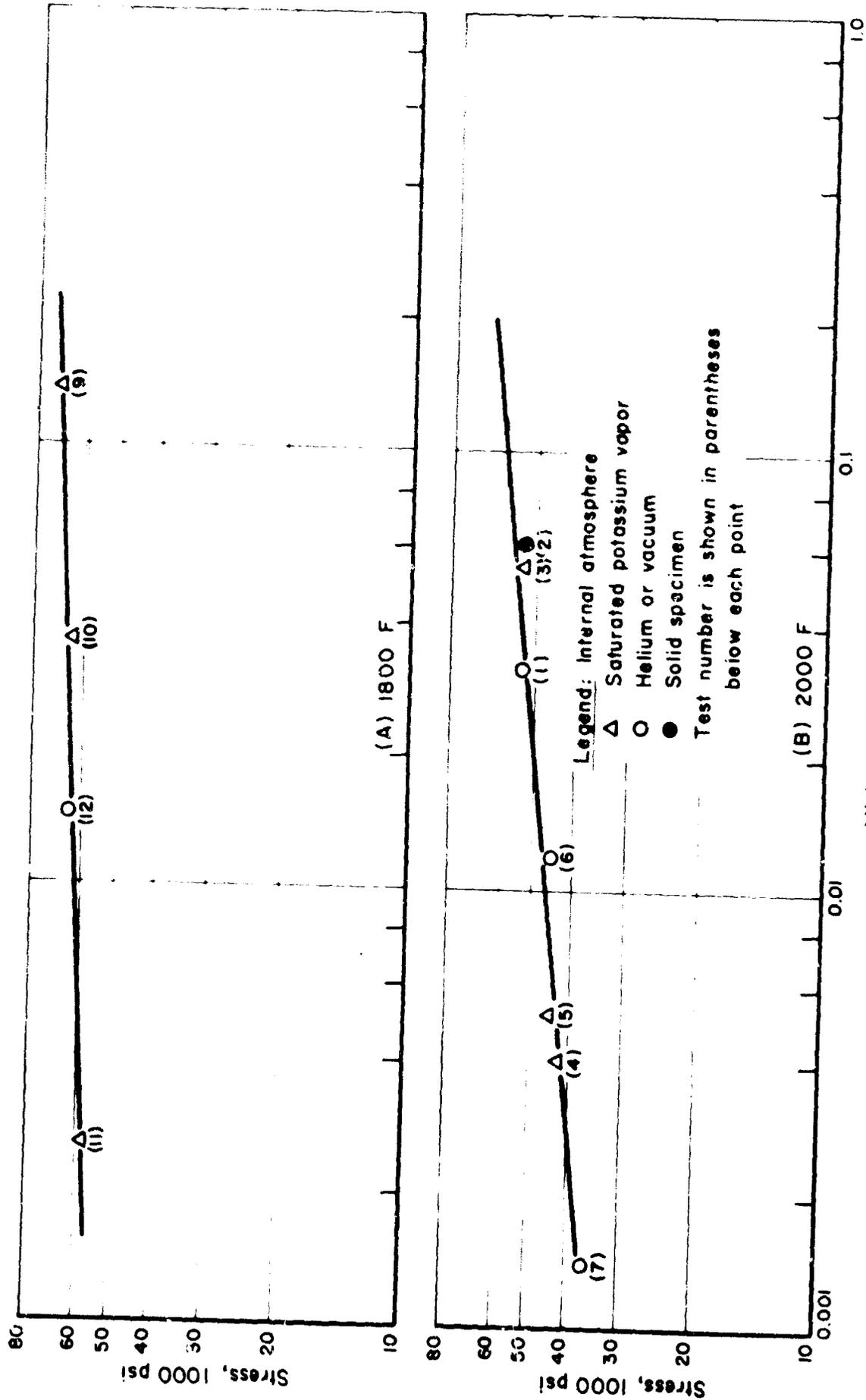


FIGURE 8. STRESS VERSUS MINIMUM CREEP RATE FOR STRESS-RELIEVED TZM ALLOY AT 1800° AND 2000°F

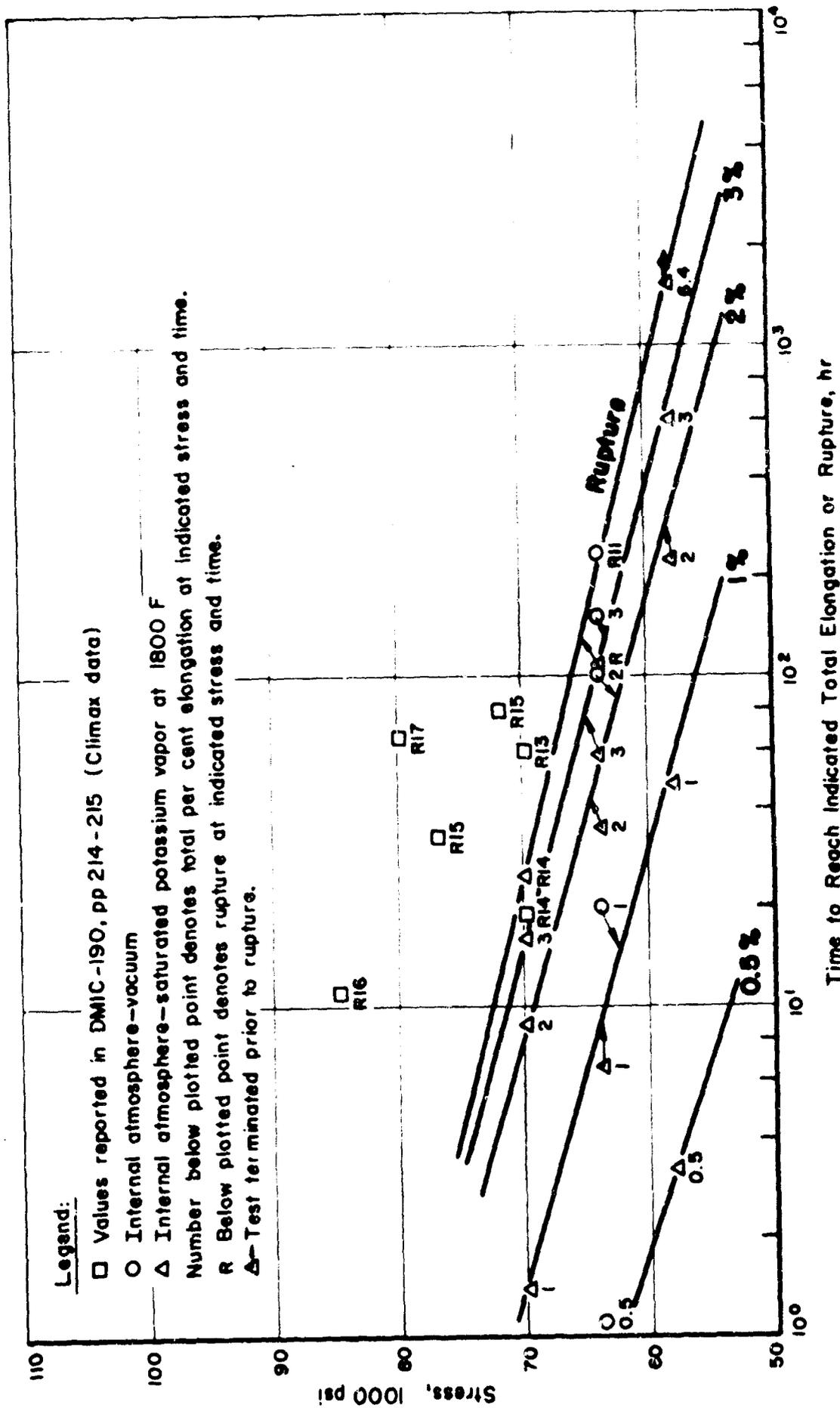


FIGURE 9. DESIGN CURVES FOR STRESS-RELIEVED TZM ALLOY AT 1800°F

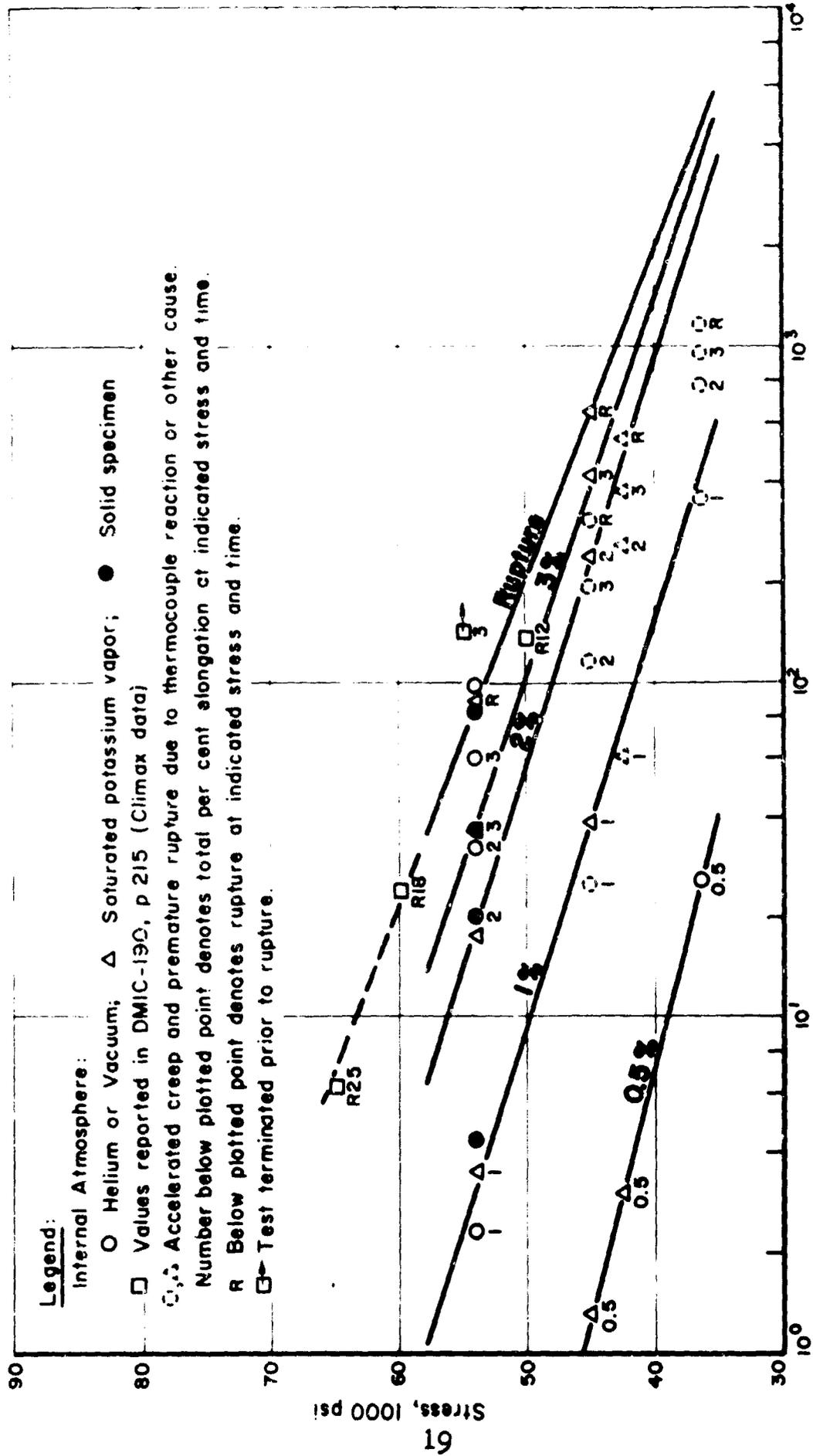


FIGURE 10. DESIGN CURVES FOR STRESS-RELIEVED TZM ALLOY AT 2000°F

thermocouple, undoubtedly because the bead was separated from the TZM surface by a double thickness of tantalum foil, whereas the ends had only a single-thickness wrapping. The reaction zones were insignificant in specimens that had been tested at 1800°F.

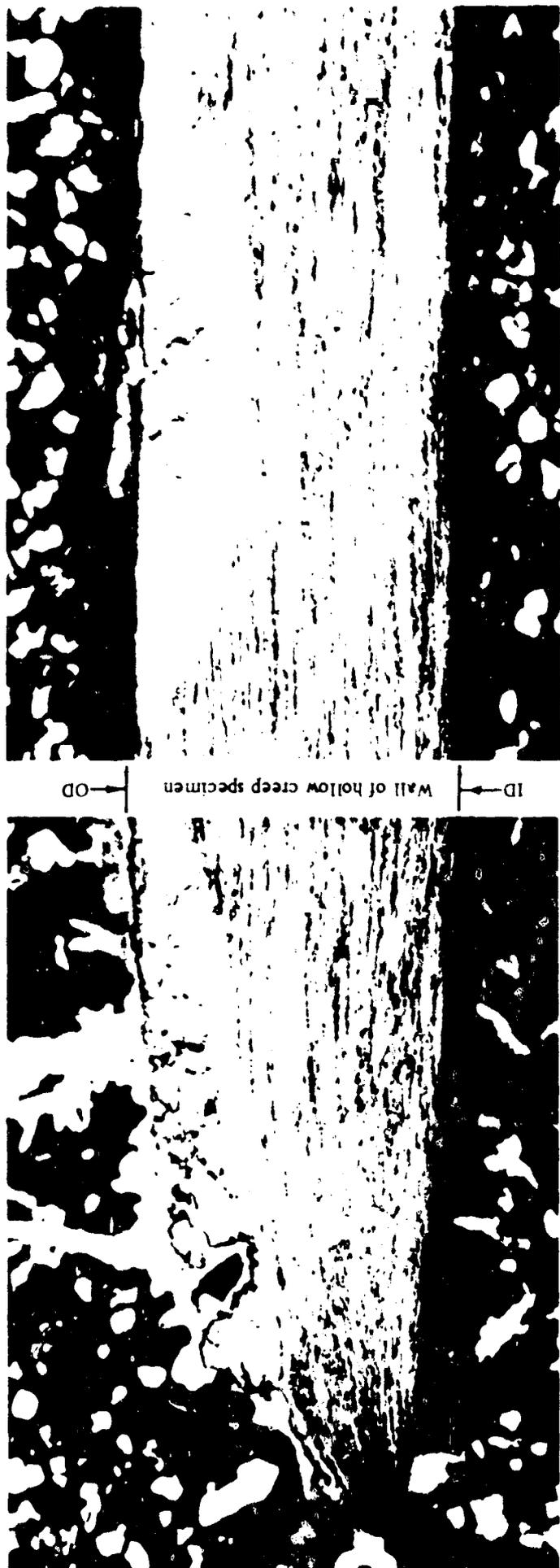
Figure 11 shows photomicrographs of sections of a specimen where reactions with the thermocouple beads had occurred. The reaction zones are sharply defined by the recrystallized grain structure. It was not considered worth while to do any detailed analytical work on the reaction products, since the problem can be circumvented in any future tests by inserting a ceramic barrier under the thermocouple bead. A reasonable guess is that the nickel in the thermocouple wires (Chromel is 90 Ni - 10 Cr and Alumel is 94 Ni - 3 Mn - 2 Al - 1 Si) diffused through the tantalum foil and into the surface of the TZM, lowering the recrystallization temperature in the Ni - Mo alloy region to below the 2000°F test temperature.

The recrystallized zones have significantly lower strength than the parent TZM. In two of the specimens (Tests 4 and 7), rupture occurred directly through such reaction zones. One of these is shown in Figure 11a, and Figure 11b shows how the grain boundaries in the recrystallized area separate under the tensile stress.

Since the reaction involves highly localized solid-state diffusion and subsequent recrystallization of the altered alloy, both of which are time-dependent phenomena at a given temperature, it would not be expected to influence the gross creep behavior until the reaction had progressed to a considerable extent. Thus, Tests 1, 2, and 3 (Figure 7) are probably not affected by this phenomenon, nor are the first 150 hours or so of Tests 4, 5, and 7. Further, since Specimen 5 did not fail through a reaction zone, its creep curve is very likely valid throughout. However, in Tests 4 and 7 where failure occurred through reaction zones, third-stage creep and rupture were undoubtedly accelerated by the thermocouple reactions. This explains why rupture occurred earlier in Test 4 than in Test 5, even though the stress was lower in Test 4.

The possibility that the diffusion reactions altered the thermocouple calibrations was investigated by calibrating a thermocouple from a particularly severe reaction zone after the creep test. It was found to be well within the tolerance, reading only 5°F low at 1983°F, as tabulated below.

Standard temp, °F	1983	1832	1578	1459	1320	1167	990	922
Indicated temp, °F	1978	1831	1578	1459	1320	1167	990	921
Error, °F	-5	-1	0	0	0	0	0	-1



50X Murakami's Etch
 a. Ruptured End
 b. Other End of Same Specimen

This is one of two specimens which broke at a reaction zone. Irregular white layer on OD is nickel plate applied to protect edge during polishing.

Note grain-boundary cracks and piece of tantalum foil wrapping on OD.

FIGURE 11. LONGITUDINAL SECTIONS THROUGH ZONES WHERE CHROME-ALUMEL THERMOCOUPLE BEADS REACTED WITH TZM IN SPECIMEN 7

C. Crystal Deposits

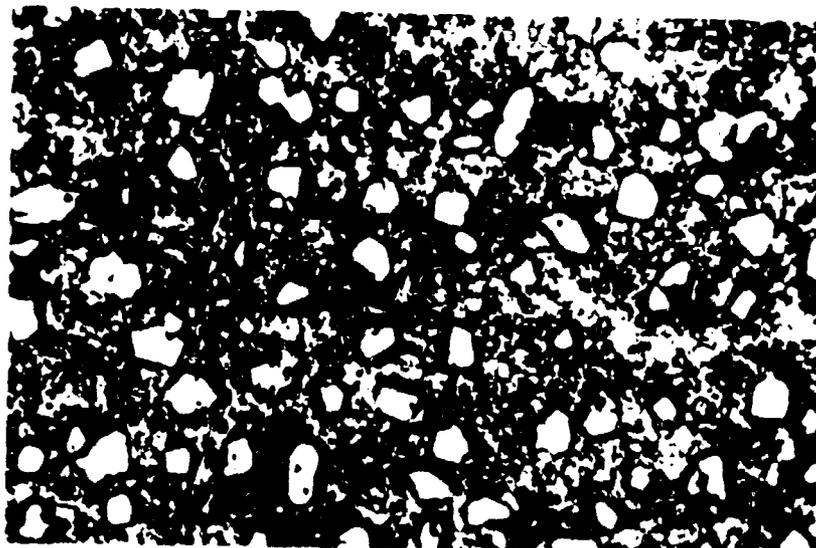
It should be noted from Table 1 that, with the exception of Specimen 7, all hollow specimens suffered an increase in the surface roughness of their bores. In general, the potassium vapor-exposed surfaces were roughened more than the vacuum- or helium-exposed surfaces. Specimen 12 appears to be an exception, but actually its bore had been exposed briefly to 1800°F potassium vapor before Test 12 was run. Originally, Specimen 12 had been charged with potassium and brought up to 1800°F in the vacuum-creep furnace in preparation for Test 11. However, before the stress was applied, a crack developed in the threads. It was feared that the crack would propagate to the interior wall. If this had occurred, the potassium vapor would have had unobstructed passage to the furnace interior and the test would have been aborted. Therefore the specimen was salvaged by drilling out an end plug, cleaning the bore with alcohol, and utilizing it for Test 12 (vacuum) instead of Test 11. It was felt that the crack did not require repair since there was a sufficient number of sound threads remaining to grip the specimen for the test.

After the tests, the specimens were cut in half longitudinally and their interior surfaces examined. All potassium-exposed specimens showed a slight polishing in the short liquid-contacting zone at the bottom but no well-defined liquid-vapor interface line. Rather, the surface appearance changed gradually from bright, where the liquid had been, to dull in the vapor region. In the three specimens that had been exposed to 2000°F potassium (Tests 3, 4, and 5), this dull finish changed to an irregular satin texture in the thin-walled gauge section. Microscopic examination of this satin finish revealed that it was caused by deposited crystals, mostly metallic. Specimens that had been tested in vacuum did not show such deposits.

Representative crystal deposits from Test 5 (2000°F, 641.3 hours) are shown in Figure 12. Microprobe analysis showed the metallic crystals to be 99 plus percent molybdenum. They were tightly adherent to the TZM surface. The nonmetallic needles, which were found only in one isolated region (Figure 12b), were identified by x-ray diffraction as K_2MoO_4 .

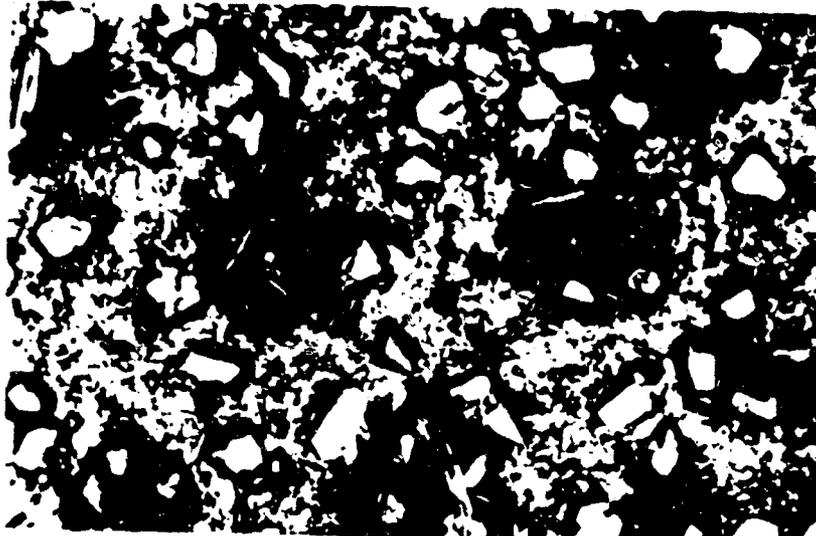
Crystal deposits, much finer and sparser, were also observed in specimens from the short-time 1800°F Tests 8, 9, and 10; and the largest, most concentrated crystals of all were found in the specimen from the 1800°F Test 11. This latter test was discontinued after 1.539 hours, with the specimen well into third-stage creep, so that the specimen could be sectioned and the potassium removed without disrupting the deposits.

As with the 2000°F specimens, the one from Test 11 showed an irregular pattern of deposition over the entire gauge section, with the heaviest concentration of crystals in a zone just above



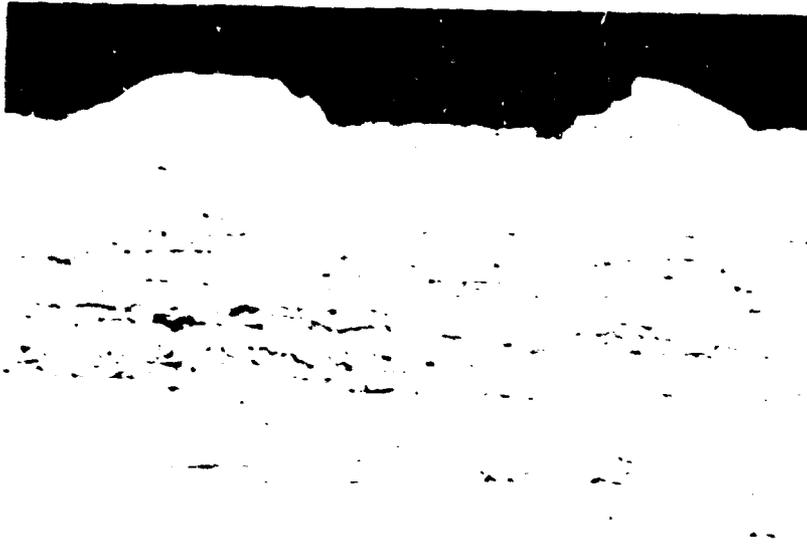
250X

a. Region of Greatest Concentration of Metallic Crystals



250X

b. Region Showing Clusters of Nonmetallic Needles Among Metallic Crystals



500X Murakami's Etch

c. Cross Section of Two Metallic Crystals on ID Surface

FIGURE 12. CRYSTAL DEPOSITS FOUND ON ID SURFACE OF SPECIMEN 5, WHICH RUPTURED AFTER 641.3 HOURS AT 2000 PSI UNDER 45,000 PSI STRESS



250X
24

a. Heavy Metallic Crystal Deposits



50X

b. ID Surface in Region of Etched Band (Specimen Axis Vertical)



100X

Section A-A
(As Polished)
c. Cross Section of Etched Band

FIGURE 13. CRYSTAL DEPOSITS AND ETCHED BAND ON ID SURFACE OF SPECIMEN 2 FROM TEST 11, WHICH RAN 1539 HOURS AT 1800°F UNDER 64,000-PSI STRESS

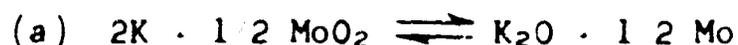
the bottom fillet. These crystals can be seen in Figures 13a and b. A well-defined circumferential ring about 20 mils wide, passing through this heavy deposition zone, was found under the microscope to be an area from which metal had been leached, as is evident in the cross-sectional view, Figure 13c. It is likely that this highly localized band was the source of much of the metal in the deposited crystals.

Similar circumferential bands were observed in all specimens tested with potassium inside. Some were scarcely more than a tarnish ring, flanked by very tiny crystals; others consisted of a smooth band bordered on one or both sides by a dense, narrow ring of metallic crystals. It appears that the locations of these rings on the specimen bores are associated with the positions of the molybdenum wire used to hold the tantalum foil and thermocouples in place (see Figure 5). This, together with the polished appearance of the liquid-contacting end and the crystal deposition in the thin-walled region, suggests a temperature-gradient mass-transfer mechanism.

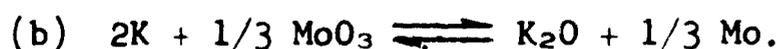
It is difficult to see how any sizable temperature gradient ($\frac{dt}{dl}$) can exist in the walls of a high-thermal-conductivity specimen during a creep test. However, it is conceivable that gradients within the specimen length of only a few degrees Fahrenheit could produce the deposits observed. From the specimen and pull-rod geometry and the furnace arrangement, it is possible that the grip ends of the specimen were hotter than the gauge length. In addition, because of the more intimate contact of the tantalum foil with the specimen surface under the place where the molybdenum wire was wound, heat radiated from the furnace to the foil was transferred to the specimen surface in this region, resulting in a local hot ring. This effect was aided by the fact that the molybdenum can absorb radiant heat more readily than tantalum by virtue of its higher emissivity (approximately 0.13 versus 0.075 to 2000°F).

Unless the boiling-refluxing action inside a specimen were accompanied by violent splashing, the observed crystal deposition would have had to take place from the vapor phase. In general the deposition patterns suggest that this (vapor phase deposition) was the case. Without a detailed study, it is not possible to spell out the mass-transfer process. There are a number of possibilities. A plausible one is that some potassium compound reacted with the TZM wall in a hot region, forming a volatile molybdenum compound which was reduced by potassium vapor in a cooler zone, depositing free molybdenum and returning the potassium compound to the hot zone to pick up more molybdenum.

As an example, consider the reactions



and



The free energy changes for the forward reactions, in kcal/mole of K_2O , are:

Reaction	ΔF° 1800°F	ΔF° 2000°F
(a)	+6.5	+9.5
(b)	-3	0

Assuming that the liquid region was hotter than the vapor region inside the specimen, the K_2O in the melt would react with molybdenum oxide, in accordance with the back reactions. Now, MoO_2 , which sublimates at 2012°F, has a relatively high vapor pressure at the test temperatures, as does MoO_3 . Consequently, a fraction of these oxide species would be transmitted to the vapor space, where the temperature is lower and the back reactions are less favored. Here, the molybdenum oxide vapors would be reduced by the potassium vapor in accordance with Forward Reactions (a) and (b), leaving molybdenum to crystallize on the cooler walls and freeing the potassium oxide to start the cycle again in the hotter liquid zone.

Fortunately, reactions that compete with Reactions (a) and (b) are much more favorable thermodynamically, thus retarding the mass-transfer processes. For example, MoO_3 and MoO_2 reacting with potassium liquid or vapor are much more likely to form K_2MoO_4 than K_2O , in accordance with the following:

Reaction	ΔF° , kcal Mole of K_2MoO_4	
	1800°F	2000°F
$2K + 2MoO_2 \longrightarrow K_2MoO_4 + Mo$	-74	-73
$2K + 2MoO_3 \longrightarrow K_2MoO_4 + MoO_2$	-126	-124
$2K + 4/3 MoO_3 \longrightarrow K_2MoO_4 + 1/3 Mo$	-108	-106

The K_2MoO_4 , which is molten above 1700°F, is apparently thermally stable at 2000°F and not readily reduced; therefore, it would be expected ultimately to tie up most of the oxygen of the system.

It should be emphasized that the above-described mechanism of transport through oxidation is only one of a variety of possibilities. The concept of simple K-Mo solution-precipitation cannot be ignored. The solubility of molybdenum in potassium at the temperatures encountered is small but finite. In a boiling-refluxing system, the refluxing potassium could dissolve molybdenum from local regions on the walls and leave crystals behind as the potassium is re-evaporated. The presence of "erosion tracks" on the ID surfaces of some specimens and the concentration of deposits above and below the hot bands tend to support this concept.

Since the kinetics of this system are not readily explainable and the anticipated life time (10,000 hours) of the components to be fabricated from this alloy is much greater than the test times experienced, a program was immediately initiated to determine the causes of the mass-transfer mechanism and the means by which it might be circumvented. These tasks will be accomplished prior to the initiation of any creep tests of longer duration.

D. Corrosion Effects

A search was made for metallographic evidence of corrosive attack other than hot-zone leaching and crystal deposition. Except for localized dissolution and deposition as shown in Figure 13 (the severest case found), the overall post-test surfaces and grain structures were the same as those of the pretest TZM. The close similarity between Figures 14(a) and 14(b) illustrates this.

E. Creep-Rupture Behavior

Comparison of the deformation-time curve in Figure 6 for Test 10 with that for Test 12 (the same stress and temperature) shows the potassium-exposed specimen to have a higher creep rate and shorter rupture life than the inert-atmosphere specimen. However, the reverse is true when Tests 5 and 6 are compared in Figure 7. This inconsistency seems to be the result of simple data scatter, rather than any real effects of environment.

The latter conclusion was reached from careful study of Figures 8, 9, and 10. Figures 8(a) and 9 correlate all the 1800°F test results, and Figures 8(b) and 10 correlate all 2000°F test results, with allowances for the accelerated creep in the later stages of Tests 4 and 7, owing to thermocouple reactions. These curves show that any influence the potassium vapor may have had on the stress-rupture behavior of the TZM in these experiments was small compared with that of other factors contributing to scatter in the data. The inert-atmosphere points seem to be more or less randomly interspersed among the potassium-vapor points.

The six 1800°F stress-rupture points from DMIC-190, plotted in Figure 9 for comparison purposes, show a great deal more scatter than do the results of the present investigation. Either the TZM material, the test conditions, or both were not consistent in the Climax tests. However, since five of the Climax points lie above the rupture curve in Figure 9, the material used by Climax must have been more creep-resistant. The Climax stress-rupture at 2000°F (Figure 10) show considerably better alignment with the newly generated 2000°F rupture curve.



500X Murakami's Etch

a. ID Surface and Grain Structure of Untested Specimen



500X Murakami's Etch

b. ID Surface and Grain Structure of Specimen 5 After 641.3-Hr Exposure to Potassium Vapor at 2000 F Under 45,000-Psi Stress

FIGURE 14. COMPARISON OF PRE- AND POST-TEST MICRO-STRUCTURES OF STRESS-RELIEVED TZM ALLOY

SECTION VI - CONCLUSIONS

On the basis of the results of this study, the following conclusions can be drawn regarding the effect of potassium on the behavior of stress-relieved TZM alloy during 1800° and 2000°F creep tests:

- (1) The 1000-hour creep-rupture behavior is not influenced significantly by exposure to potassium vapor during creep testing at the above test temperatures.
- (2) Nonisothermal TZM surfaces in contact with 1800° or 2000°F saturated potassium vapor can undergo hot-zone leaching and cooler-zone crystal deposition. Apparently small temperature gradients will suffice since each of the three specimen thermocouples indicated only minute temperature variations within the specimen.
- (3) The severity of the mass transfer appears to increase with increasing maximum temperature and duration of the exposure.
- (4) Extreme care should be practiced in extrapolating the resultant data until the nature of the mass-transfer mechanism is ascertained. If the results of the newly initiated mass-transfer investigation indicate that this mechanism can be circumvented, the results will have to be substantiated by future creep tests of longer duration.

SECTION VII - REFERENCES

1. Oak Ridge National Laboratory Report 2622 (1959).
2. Technical Documentary Report No. ASD-TDR-63-270, Part II (Nov. 1963).