OAK RIDGE NATIONAL LABORATORY LIBRARY
3 4456 0021308 9

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

ORNL-3569
UC-25 – Metals, Ceramics, and Materials
TID-4500 (29th ed.)

EFFECT OF DEGREE OF VACUUM ON THE SLOW-BEND CREEP BEHAVIOR OF COLUMBIUM–0.6% ZIRCONIUM AT 1000°C

T. K. Roche

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this document, send in name with document and the library will arrange a loan.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

ORNL-3569

Contract No. W-7405-eng-26

METALS AND CERAMICS DIVISION

EFFECT OF DEGREE OF VACUUM ON THE SLOW-BEND CREEP BEHAVIOR OF COLUMBIUM-0.6% ZIRCONIUM AT 1000°C

T. K. Roche

JUNE 1964

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

OAK RIDGE NATIONAL LABORATORY LIBRARY
3 4456 0021308 9

EFFECT OF DEGREE OF VACUUM ON THE SLOW-BEND CREEP BEHAVIOR OF COLUMBIUM–0.6% ZIRCONIUM AT 1000°C

T. K. Roche

ABSTRACT

Columbium and its alloys are subject to interstitial contamination in vacuum environments and the interstitials, in turn, influence the mechanical properties of these materials. To investigate creep behavior during contamination, the deflection rates of cantilevered Cb–0.6% Zr specimens, loaded to an initial outer fiber stress of 12,500 psi, were determined at pressures ranging from approximately 10^{-7} to 10^{-5} torr for a test period of 504 hr at 1000°C.

A typical deflection-time curve exhibited an approximately linear "steady-state" deflection rate during the early stages of test followed by a continuously decreasing rate for the duration of the test. It was observed that systematic increases of the test pressure progressively weakened the alloy during the "steady-state" stages and strengthened the alloy during the latter test stages. At a test pressure in the range of 1.6 to 6×10^{-5} torr, the alloy was significantly weakened at a still later stage of testing. To further demonstrate the effect of the test pressure, it was possible to accelerate or decelerate the deflection rate of a single specimen by increasing or decreasing the test pressure.

The observed slow-bend creep behavior has been correlated with the contamination experienced by the alloy from the residual gases in the vacuum system. This correlation was supported by posttest chemical analyses for interstitials and metallographic observations.

It was concluded that the test pressure is an important variable influencing the slow-bend creep behavior of Cb–0.6% Zr.

INTRODUCTION

Interstitial elements, added intentionally or from environmental contamination, markedly affect the properties of columbium and its alloys. Even in vacuum, residual gases, such as water vapor, O_2, N_2, CO, CO_2,

and hydrocarbons, constitute potential sources of contamination. The presence of these gases can result from atmospheric leaks into the system, outgassing from interior surfaces, diffusion through the system walls, and release of gases from the vacuum pump.

Mechanical property studies on columbium and its alloys are most frequently carried out in vacuum systems over fairly wide pressure ranges. Although the pressure variable with its associated contamination potential can affect strength values, there has been little, if any, systematic work carried out to determine the effect of this test variable on the mechanical properties of these materials. Therefore, the purpose of this study was to investigate the effect of test pressure in the approximate range of 10^{-7} to 10^{-5} torr on the strength of Cb–0.6% Zr in a cantilever beam slow-bend creep test.

EXPERIMENTAL APPARATUS AND PROCEDURE

Cantilever beam bend tests have been used for qualitatively evaluating the creep strength of materials. An apparatus originally designed and constructed for this purpose was used for the present investigation and is shown schematically in Fig. 1. The system was essentially all-ceramic, made up of a primary mullite tube to which were attached pyrex extensions with standard ground joints at the ends. An inner mullite tube, serving as a pedestal for the specimen holder, was supported by the ground joint of the load-containing assembly at the bottom of the system. A mullite tube for a recording thermocouple was brought within 1/4 in. of the specimen through a cap at the top of the system.

Vacuum ports, located at both top and bottom, were each connected to a 25-liter/sec glass diffusion pump backed with a mechanical pump. A liquid-nitrogen cold trap was located between each diffusion pump and the system. Pressure in the system was monitored with an ionization gage on each vacuum port. Variable system pressure was obtained through regulation of the power input to the pump heaters. The variation in system pressure with diffusion pump amperage is shown in Fig. 2. These data were obtained at 1000°C with no specimen in the apparatus.

For conducting a bend test, the specimen (1.156 × 0.250 × 0.040 in.) was fixed in the molybdenum specimen holder with a molybdenum fastener

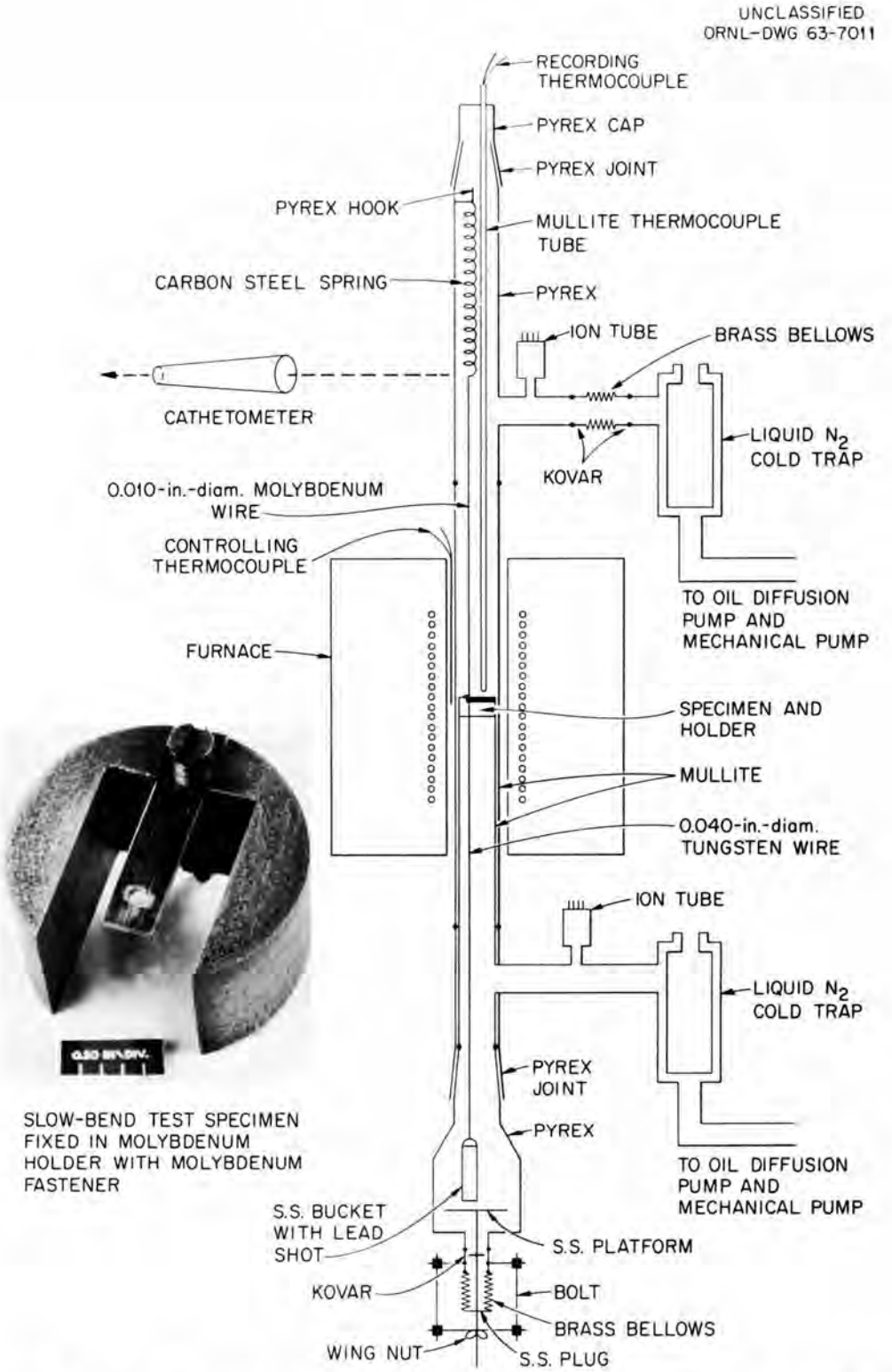


Fig. 1. Schematic Diagram of Cantilever Beam Slow-Bend Test Apparatus.

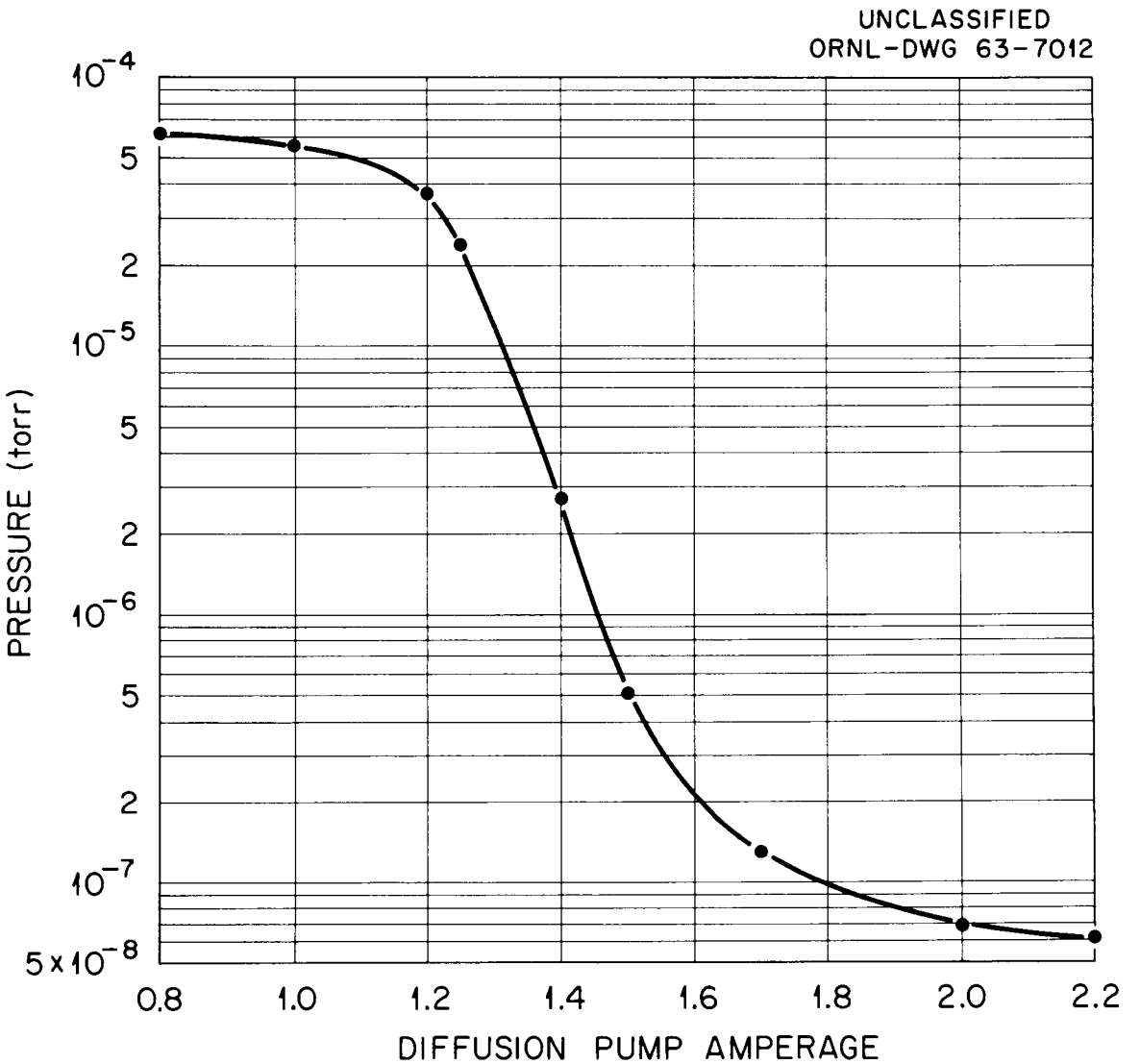


Fig. 2. Variation in System Pressure with Diffusion Pump Amperage at 1000°C.

(see Fig. 1 insert). The load required for the initial outer fiber stress was calculated and applied by means of a bucket weighted with lead shot. The bucket hung from a 0.040-in.-diam tungsten wire attached through the hole in the end of the specimen. Through this same hole was attached a 0.010-in.-diam molybdenum wire which was directed toward the top of the system and held upright by means of a flexible spring prepared from 0.005-in.-diam piano wire. The deflection of the specimen was measured within ±0.001 in. by means of a cathetometer by observing the downward movement of the 0.010-in.-diam molybdenum wire relative to a fixed point on the thermocouple protection tube. The load, with the exception of the tungsten wire, could be removed from the specimen during heat-up by means of a platform activated through a brass bellows in the load-containing assembly.

Heat-up times to 1000°C were on the order of a week to prevent excessive pressure rise in the system by a rapid heating rate. Greatest outgassing occurred between the temperatures of 200 and 500°C when the pressure would rise to 1 to 2×10^{-5} torr for short periods of time. A pressure of less than 1×10^{-5} torr was maintained between 500 and 1000°C. Upon reaching the test temperature, the pressure was adjusted, and the load was applied to the specimen by retracting the platform by means of a wing-nut. Zero deflection of the specimen was recorded at this time.

Prior to bend testing at 1000°C with an initial outer fiber stress of 12,500 psi, the Cb–0.6% Zr specimens were vacuum annealed 2 hr at 1200°C. To determine the effect of pressure, tests were carried out over three ranges: 7×10^{-8} to 3×10^{-7} torr, 3.2 to 7.4×10^{-6} torr, and 1.6 to 6×10^{-5} torr for a test period of about 500 hr. As the deflection of the specimens was found to be dependent upon the extent of interstitial contamination during test, the effect of a precontamination treatment in the pressure range of 10^{-5} torr on the deflection behavior in this same pressure range was also determined. In addition, the effect of varying the pressure during a single test was investigated. Finally a bend test was conducted to demonstrate the protection of a specimen against contamination by wrapping with 0.003-in.-thick molybdenum foil.

After bend testing, most of the specimens were sectioned longitudinally for metallographic examination and chemically analyzed for interstitials. The portion of the specimen which contacted the molybdenum specimen holder was discarded from the coupon for interstitial analysis. To aid in distinguishing various phases present in the specimens, a staining technique was used.[1,2] This consisted of making a polished metallographic specimen the anode in an electrolytic cell with an electrolyte of 5 g oxalic acid, 5 g citric acid, 5 ml phosphoric acid, 10 ml lactic acid, 35 ml water, 60 ml ethyl alcohol, and a stainless steel cathode. Twenty volts were applied across the cell for approximately 0.5 sec. This treatment stained the matrix blue, CbO a lighter shade of blue, and columbium carbides and/or nitrides orange-pink. The presence of CbO was also confirmed by x-ray diffraction. Specimens with only ZrO_2 precipitated in the matrix were etched chemically with 10 ml sulfuric acid, 10 ml nitric acid, 25 ml hydrofluoric acid, and 50 ml water.

In the pressure range of 10^{-5} torr, pronounced contamination of the specimen resulted in distinctive effects on the deflection rate. To determine if these were related to changes in contamination rate with time, balance techniques were used to establish the contamination rate curve in this pressure range. The data were obtained on a 0.040-in.-thick specimen of known area suspended from an Ainsworth semi-microbalance into a mullite tube which was enclosed in a furnace. The increase in weight of the specimen was automatically recorded for approximately 500 hr at 1000°C. Vacuum techniques for this system were similar to those used for the bend test apparatus except, in this case, only a single pumping port was provided.

---

[1]E. Ence and H. Margolin, J. Metals 6, 346–48 (March 1954).

[2]R. S. Crouse, "Identification of Carbides, Nitrides, and Oxides in Columbium by Anodic Staining," paper presented at the 16th AEC Metallography Group Meeting, Hanford Atomic Products Operation, Richland, Washington (March 1962).

RESULTS AND DISCUSSION

Effect of Test Pressure

The base pressure of the system was in the range 7×10^{-8} to 3×10^{-7} torr, and the deflection-time curve obtained in this pressure range was used as the reference to which curves established at higher pressures were compared. Figure 3 shows the deflection-time curves for specimens tested at the base pressure as well as 3.2 to 7.4×10^{-6} torr and 1.6 to 6×10^{-5} torr. For these conditions, the specimens experienced a period of "steady-state" deflection during the early stages of test followed by a decrease in the deflection rate.

Relative to the reference test, it was found that a systematic increase in the test pressure resulted in progressive weakening (i.e., increase in the deflection rate) of the alloy during the "steady-state" period of deflection. Typical "steady-state" deflection rates as shown in Fig. 3 are listed in Table 1. For the period following the "steady-state" deflection rate, the opposite effect was observed (i.e., increasing the test pressure resulted in strengthening of the alloy).

Table 1. "Steady-State" Deflection Rates for Cb–0.6% Zr Slow-Bend Tested at 1000°C and 12,500 psi Initial Outer Fiber Stress

Curve[a]	Test Pressure (torr)	Period of "Steady-State" Deflection (hr)	Deflection Rate (in./hr)
			$\times 10^{-4}$
A	7×10^{-8} to 3×10^{-7}	55 to 225	1.33
B	3.2 to 7.4×10^{-6}	50 to 225	1.77
C	1.6 to 6×10^{-5}	7.5 to 105	2.94

[a]See Fig. 3.

In the test conducted at 1.6 to 6×10^{-5} torr, a very rapid increase in the deflection rate occurred about midway through the test period. This coincided with an inadvertent increase in the system pressure to 1.6×10^{-4} torr. Since no data were recorded during this time, additional tests were conducted in the 10^{-5} torr pressure range which confirmed the existence of a highly weakened alloy as will be described subsequently.

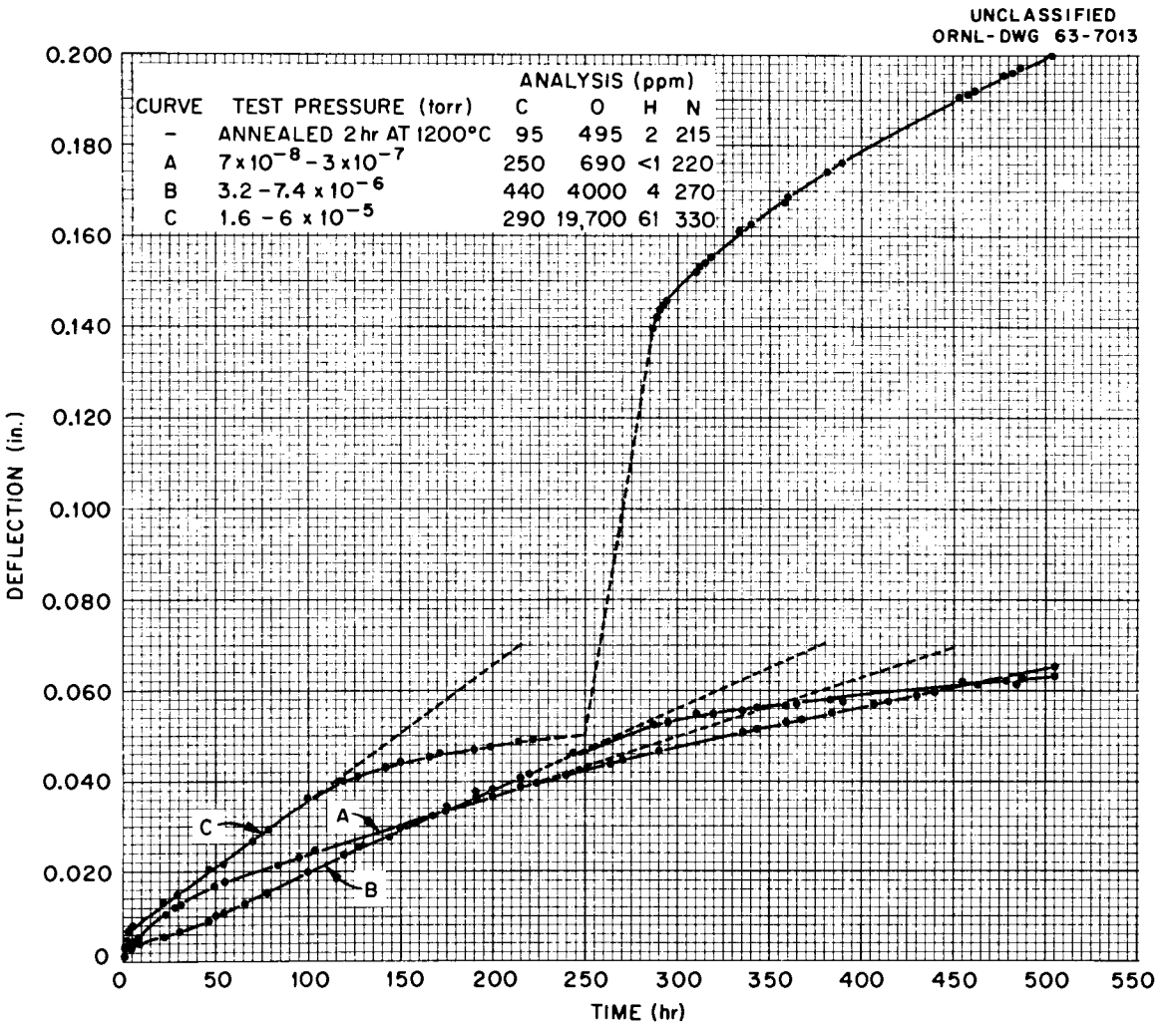


Fig. 3. Deflection-Time Curves for Cb–0.6% Zr Slow-Bend Tested at 1000°C and 12,500 psi Initial Outer Fiber Stress.

The extent of interstitial contamination of the test specimens is presented in Table 2. For comparative purposes, the analysis of the annealed material and that of a specimen taken through the heat-up schedule to 1000°C in the same equipment, but not bend tested, are also tabulated. From these data, it is apparent that the major fraction of the total carbon contamination occurred on heat-up of the specimens to the test temperature. Increases in oxygen content as well as the slight increases in nitrogen content were dependent upon the test pressure.

Table 2. Pretest and Posttest Chemical Analyses and Weight Change Data on Cb–0.6% Zr Slow-Bend Specimens

Test Temperature:	1000°C
Initial Outer Fiber Stress:	12,500 psi
Test Duration:	504 hr
Thickness of Specimen:	0.040 in.
Approximate Exposed Surface Area of Specimen:	0.525 in.^{2} (3.39 cm^2)

Specimen	Analysis				
	Zr (wt %)	C (ppm)	O (ppm)	H (ppm)	N (ppm)
Annealed 2 hr at 1200°C	0.60 ± 0.03	95	495	2	215
Heated to 1000°C in bend-test rig, but not tested	-	290	540	3	230
Bend tested at 7×10^{-8} to 3×10^{-7} torr	-	250	690	< 1	220
Bend tested at 3.2 to 7.4×10^{-6} torr	-	440	4000	4	270
Bend tested at 1.6 to 6×10^{-5} torr	-	290	19,700	61	330

A determination of residual gas species in a mullite-pyrex system at 1200°C and in the pressure range of 10^{-6} to 10^{-5} torr has been made by Inouye.[3] The principal gases were found to be primarily hydrogen and water vapor with minor amounts of CH_4, CO_2, N_2 + CO, other hydrocarbons, Ar, and O_2. Assuming the presence of these same gases in the bend-test apparatus, the sources of oxygen, carbon, and nitrogen contamination are apparent.

[3]H. Inouye, "Contamination of Refractory Metals in High Vacua," Metals and Ceramics Div. Ann. Prog. Rept. May 31, 1963, ORNL-3470 (Nov. 1963).

Typical posttest microstructures of the bend specimens, as shown in Fig. 4, were markedly dependent upon differences in interstitial content. The pretest anneal at 1200°C promoted precipitation of a fine dispersion of ZrO_2 which is illustrated in Fig. 4a. Taking a specimen through the heat-up schedule to 1000°C but not bend testing did not alter the apparent microstructure of the alloy relative to the as-annealed material. The same was true for the specimen tested in the range of 7×10^{-8} to 3×10^{-7} torr, Fig. 4b. However, the specimens tested in the two higher pressure ranges contained a uniformly distributed phase, identified by staining to be a columbium carbide or nitride. This phase precipitated either at the test temperature or on cooling to room temperature, Fig. 4c and d. In addition, a gradient of CbO formed intergranularly in the specimen tested in the 10^{-5} torr pressure range, Fig. 4d. The CbO was identified both by staining and x-ray diffraction. Cracking was not found in any of the specimens.

The observed strength variations of Cb–0.6% Zr resulting from pressure changes are interpreted as follows: It is known that structural instabilities from phenomena such as phase transformations, recrystallization, and grain growth during creep testing can accelerate the creep rate of a material due to the generation of dislocations.[4,5] A similar effect can be expected from dislocations generated from precipitation of excess phases having a greater specific volume than the matrix. In the present investigation, the progressive weakening of the alloy with increasing test pressure (contamination rate) during the period of "steady-state" deflection was undoubtedly brought about by the increased rate of precipitation of ZrO_2 and probably columbium carbides or nitrides which have specific volumes greater than the matrix.

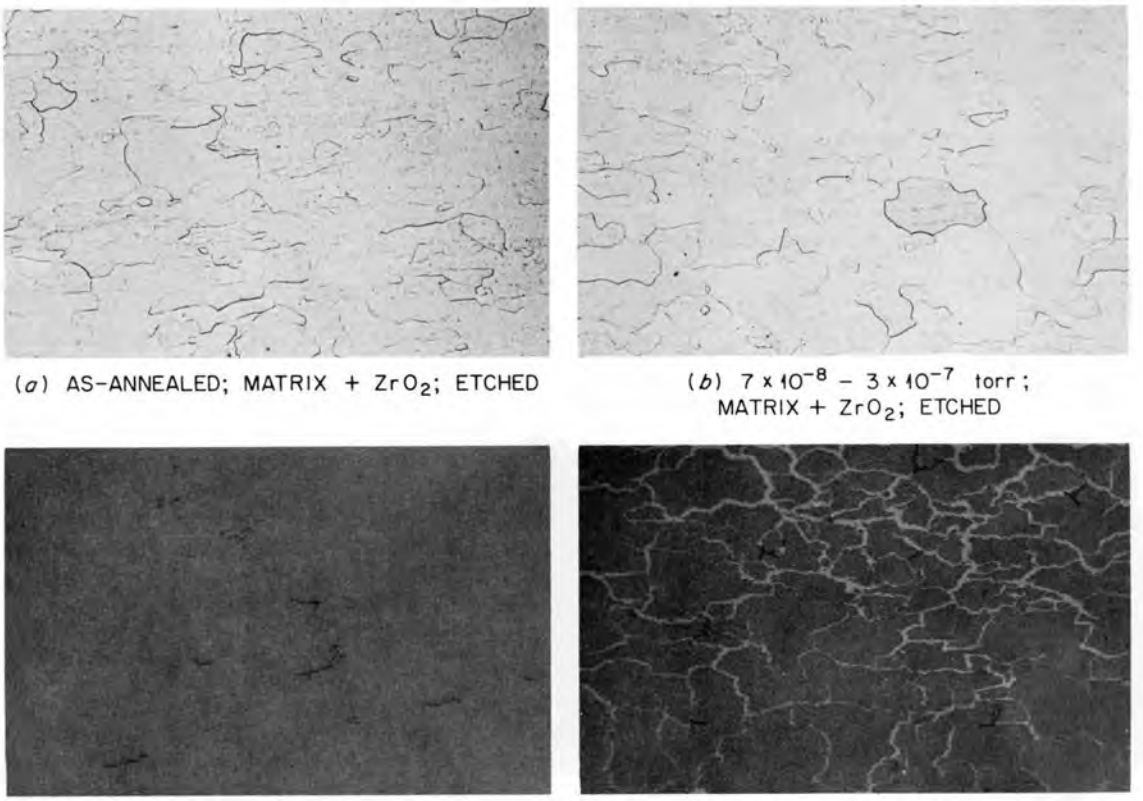
The strengthening observed subsequent to the termination of the "steady-state" period can be explained by the effects of dispersion

---

[4]G. V. Smith, Properties of Metals at Elevated Temperatures, 1st ed., pp 98–100, McGraw-Hill, New York, 1950.

[5]E. R. Parker, "Creep of Metals," p 25 in High Temperature Properties of Metals, American Society for Metals, Cleveland, Ohio, 1951.

UNCLASSIFIED
PHOTO 63601



(*a*) AS-ANNEALED; MATRIX + ZrO_2; ETCHED

(*b*) $7 \times 10^{-8} - 3 \times 10^{-7}$ torr; MATRIX + ZrO_2; ETCHED

(*c*) $3.2 - 7.4 \times 10^{-6}$ torr; MATRIX + ZrO_2 + COLUMBIUM CARBIDE OR NITRIDE; STAINED

(*d*) $1.6 - 6 \times 10^{-5}$ torr; MATRIX + ZrO_2 + CbO + COLUMBIUM CARBIDE OR NITRIDE; STAINED

Fig. 4. Columbium–0.6% Zirconium, Annealed 2 hr at 1200°C, Slow-Bend Tested 504 hr at 1000°C, 12,500 psi Initial Outer Fiber Stress in the Indicated Pressure Ranges. 500×; reduced 29%.

and possibly solid solution strengthening overriding the instabilities produced by contamination. Calculations based on the posttest analysis of the specimen tested in the 10^{-6} torr range showed an excess of approximately 1900 ppm O_2 over that required for the conversion of all the zirconium to ZrO_2. This excess oxygen would be expected to be in solution. Hobson[6] has found from lattice parameter studies that the solubility limit of oxygen in Cb–0.88% Zr was 300 ppm at 1600°C. With increasing oxygen content beyond the solubility limit, the precipitation of ZrO_2 resulted in a net decrease in the lattice parameter of the matrix due to zirconium depletion. This, in turn, permits an increase in oxygen solubility in the matrix.

The rapid increase in deflection rate of the specimen after 250 hr in the 10^{-5} torr pressure range was found to be related to the massive intergranular precipitation of CbO due to the high level of oxygen contamination. Evidence for this is presented below.

Effect of Precontamination Treatment

From the data presented, it can be seen that interstitial contamination of the alloy resulted in three major sequential effects: (1) initial weakening due to the promotion of alloy instabilities, (2) strengthening due to dispersants and possibly interstitials in solution, and (3) weakening due to the precipitation of a new phase, CbO.

It was postulated that these effects could be controlled or predicted on the basis of the extent of contamination. To corroborate this hypothesis, a specimen was precontaminated for 100 hr at 1000°C in the pressure range of 2.5 to 4×10^{-5} torr and bend tested at the same conditions with the expectation that the initial deflection rate would be lower due to dispersion and possibly solid solution strengthening. Then, if the test were continued beyond that time required to precipitate CbO, the deflection rate should accelerate to the high levels described in Fig. 3. This change should occur in about 150 hr rather than in 250 hr as for the specimen which was not precontaminated.

The results of this test are shown in Fig. 5, curve B. It can be seen that precontamination did cause marked strengthening of the alloy at the outset of the test and that the shape of the initial portion of

[6]D. O. Hobson, Aging Phenomena in Columbium-Base Alloys, ORNL-3245 (March 16, 1962).

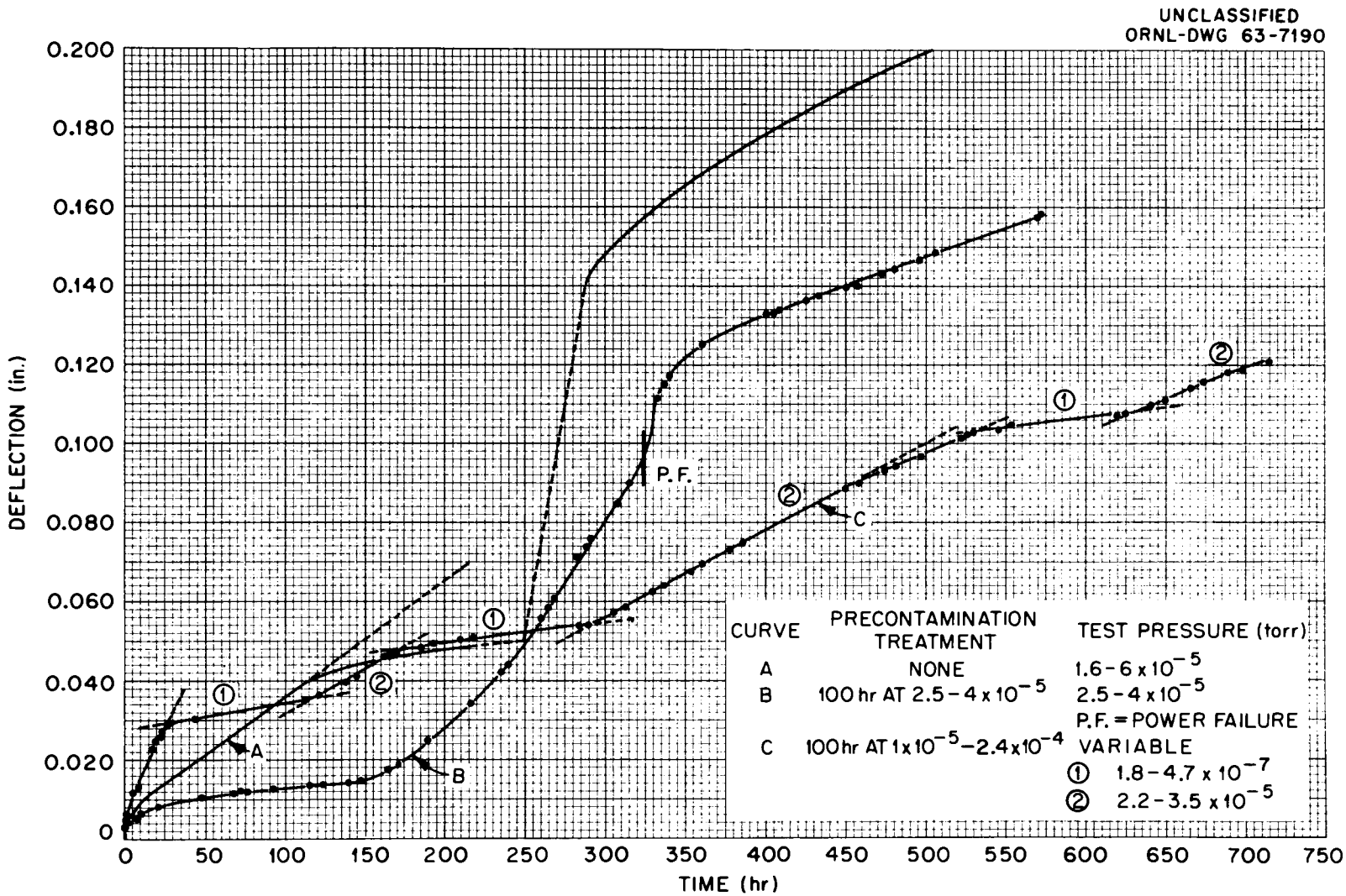


Fig. 5. Deflection-Time Curves for Precontaminated Cb–0.6% Zr Slow-Bend Tested at 1000°C and 12,500 psi Initial Outer Fiber Stress.

this deflection-time curve closely resembles the shape of curve after 100 test hours on the specimen stressed in the 1.6 to 6×10^{-5} torr pressure range without a precontamination treatment (Fig. 5, curve A). A subsequent acceleration in deflection rate also was noted for the specimen which received the precontamination treatment. In this case, the period of accelerating deflection took place during the time interval of 140 to 330 hr.

The starting time of accelerating deflection was in very good agreement with prediction, but the total duration was considerably longer than expected. An increase in system pressure to 1.6×10^{-4} torr during this period of accelerating deflection for the first specimen tested (Fig. 5, curve A) could account for its more limited duration. A point of interest is the inflection (denoted by P.F.) in the curve after 323 hr for the precontaminated specimen. This resulted from a system power failure followed by an increase in system pressure and a subsequent increase in contamination rate.

To show that the precipitation of CbO was responsible for the acceleration in the deflection rates for the tests conducted in the 10^{-5} torr pressure range, two additional tests were run – one being terminated before and the second during the period of accelerating deflection. Each of these specimens received a 100-hr precontamination treatment in the pressure range of 2 to 4×10^{-5} torr. The deflection rates checked those observed in Fig. 5, curve B, and were representative of the strengthened and weakened stages. The specimens had been exposed to the contaminating gases at 2 to 4×10^{-5} torr for a total of 174.5 and 295 hr, respectively. Posttest interstitial analyses and microstructures of these specimens are shown in Table 3 and Fig. 6. Metallographic examination showed both specimens to contain columbium carbide or nitride precipitates, but CbO was observed only in the specimen contaminated for 295 hr (195 hr under stress).

Effect of Varying Test Pressure During a Single Test

The sensitivity of the cantilever beam slow-bend test to changes in the test pressure during the course of a single test was determined and is illustrated in Fig. 5, curve C. In this case, the pressure during

Table 3. Pretest and Posttest Chemical Analyses and Weight Change Data on Cb–0.6% Zr Slow-Bend Specimens Tested in the Pressure Range of 2 to 4 × 10^{-5} torr

Test Temperature:	1000°C
Precontamination Period at Test Pressure:	100 hr
Initial Outer Fiber Stress:	12,500 psi
Thickness of Specimen:	0.040 in.
Approximate Exposed Surface Area of Specimen:	0.525 in.^{2} (3.39 cm^2)

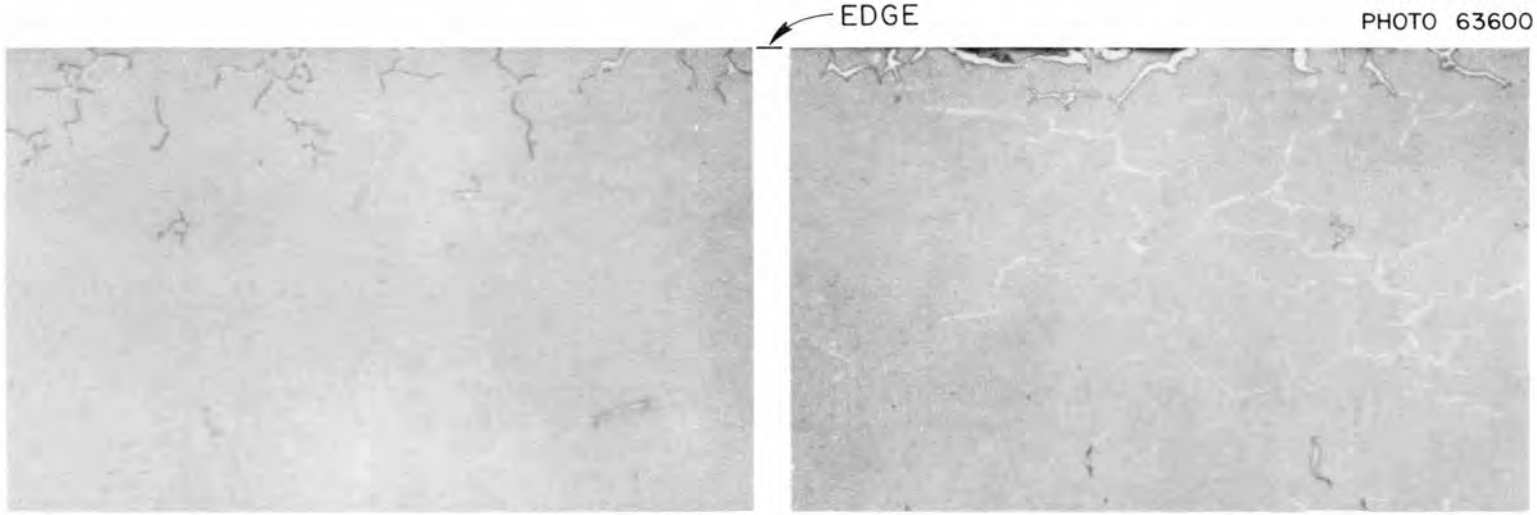
Specimen	Analysis				
	Zr (wt %)	C (ppm)	O (ppm)	H (ppm)	N (ppm)
Annealed 2 hr at 1200°C	0.60 ± 0.03	95	495	2	215
Bend tested 74.5 hr	-	300	3800	15	390
Bent tested 195 hr	-	430	7100	13	500

the 100-hr precontamination treatment ranged from 1 × 10^{-5} to 2.4 × 10^{-4} torr, a level higher than that used in previous precontamination experiments. This introduced some rather surprising behavior in the deflection-time curve for the specimen. During the initial 22.5 hr of test, the specimen deflected faster than other tests in this same pressure range.

Following the 22.5-hr period, the pressure was reduced to 10^{-7} torr and the test was continued under conditions of systematic variation in test pressures between 10^{-7} and 10^{-5} torr. The deflection-rate curve went through an inflection within a period of about 10 hr following each pressure change. The higher contamination rate in the 10^{-5} torr pressure range resulted in a higher deflection rate than was found in the 10^{-7} torr pressure range.

A total of 506 hr, including the 100-hr precontamination treatment, of high pressure time was accumulated on the specimen. Weight change measurement showed an increase of 27,280 ppm of contamination as compared to 19,574 ppm for the test carried out for 504 hr in the 1.6 to 6 × 10^{-5} torr pressure range (Fig. 5, curve A). Thus, this specimen was contaminated during the pretest contamination period to a much higher level than was experienced previously. The high deflection rate

UNCLASSIFIED
PHOTO 63600



(*a*) 74.5 hr; MATRIX + ZrO_2 + COLUMBIUM CARBIDE OR NITRIDE; STAINED

(*b*) 195 hr; MATRIX + ZrO_2 + CbO + COLUMBIUM CARBIDE OR NITRIDE; STAINED

Fig. 6. Columbium–0.6% Zirconium, Annealed 2 hr at 1200°C, Precontaminated 100 hr, Followed by Slow-Bend Testing for the Indicated Times at 1000°C, 12,500 psi Initial Outer Fiber Stress in the Pressure Range of 2 to 4 × 10^{-5} torr. 500×; reduced 19%.

for the first 22.5 hr of test could then be reasonably compared to the rapid increase in deflection rate which occurred during CbO precipitation in the other specimens tested in this same pressure range. See, for example, the period from 140 to 330 hr in Fig. 5, curve B.

Effect of Molybdenum Foil Wrapping

Inouye[7] has found that, by wrapping a 0.040-in.-thick specimen of Cb–1% Zr with 0.003-in.-thick molybdenum foil, the contamination of the specimen in the temperature range of 1030 to 1045°C at a pressure of 1×10^{-6} torr was reduced significantly. Applying these results to the present investigation, a bend test was carried out in the pressure range of 2.2 to 4.7×10^{-5} torr on a specimen wrapped with this thickness of foil. The deflection-time curve and posttest chemical analysis for this specimen were compared with those obtained on the bare specimens tested in the pressure ranges of 7×10^{-8} to 3×10^{-7} torr and 1.6 to 6×10^{-5} torr. The results are presented in Fig. 7 and Table 4. The molybdenum foil was effective in reducing contamination, thereby suppressing the weakening influence of CbO precipitation. However, the posttest chemical analysis of the wrapped specimen suggested that its deflection behavior should have resembled more closely that shown by a bare specimen tested in the 10^{-6} torr pressure range. This probably would have been the case if the load for producing a 12,500-psi initial outer fiber stress had been adjusted to account for the increased specimen thickness due to the molybdenum foil wrapping.

Contamination Rate Studies in the 10^{-5} torr Pressure Range

With CbO precipitation causing pronounced weakening of the alloy, it was of interest to determine if this effect correponded to a change in contamination rate with time in the 10^{-5} torr pressure range. The contamination and deflection-time curves in this pressure range are compared in Fig. 8. These results show the contamination rate of the specimen to be linear. The increase in weight of the specimen amounted

---

[7]H. Inouye, "The Contamination of Refractory Metals in Vacua Below 10^{-6} torr," paper presented at the Symposium on Applied Aspects of Refractory Metals, Los Angeles, California, December 9 and 10, 1963.

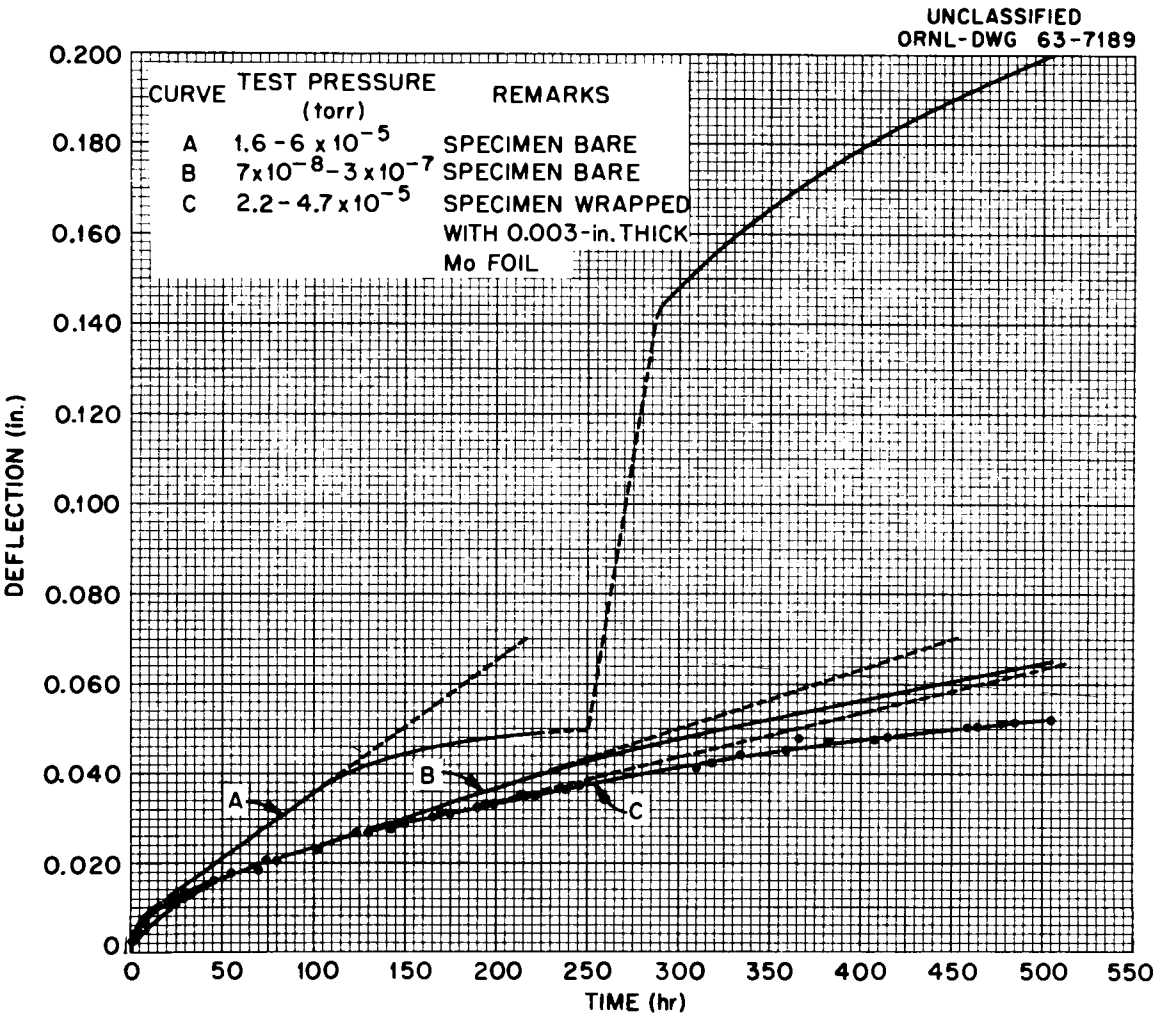


Fig. 7. Deflection-Time Curves for Bare and Molybdenum-Wrapped Cb–0.6% Zr Slow-Bend Tested at 1000°C and 12,500 psi Initial Outer Fiber Stress.

Table 4. Pretest and Posttest Chemical Analyses of Bare and Molybdenum-Wrapped Cb–0.6% Zr Slow-Bend Specimens

Test Temperature: 1000°C
Initial Outer Fiber Stress: 12,500 psi
Test Duration: 504 hr

Test Pressure (torr)	Analysis (ppm)				Remarks
	C	O	H	N	
-	95	495	2	215	Annealed standard
7×10^{-8} to 3×10^{-7}	250	690	< 1	220	Specimen bare
1.6 to 6×10^{-5}	290	19,700	61	330	Specimen bare
2.2 to 4.7×10^{-5}	250	2,300	7	360	Specimen wrapped with 0.003-in.-thick molybdenum foil

to 6.6 mg/cm^2/500 hr as compared with an increase of 7.46 mg/cm^2/504 hr for the slow-bend specimen. Therefore, the weakening of the alloy due to CbO precipitation was not related to a change in contamination rate with time.

SUMMARY AND CONCLUSIONS

The creep behavior of Cb–0.6% Zr in a cantilever beam slow-bend test at 1000°C and an initial outer fiber stress of 12,500 psi was found to be strongly dependent upon the test vacuum due to varying amounts of contamination from residual gases in this environment. The alloy was both weakened and strengthened by interstitial contamination, depending upon such variables as (1) the rate at which interstitials were added to the alloy from the test environment, (2) the solubility of interstitials in the alloy, and (3) the concentration of interstitials in the alloy at the time of application of the stress.

With the alloy initially containing 95 ppm C, 495 ppm O, 2 ppm H, and 215 ppm N, a systematic increase in the test pressure within the range 7×10^{-8} to 6×10^{-5} torr promoted an increase in contamination rate which was reflected in a progressive weakening of the alloy during the early test stages. Later the alloy was strengthened by dispersed phases such as ZrO_2 and probably columbium carbides or nitrides and possibly by interstitials in solution. This strengthening effect was more pronounced at test pressures greater than the system base pressure, 7×10^{-8} to 3×10^{-7} torr.

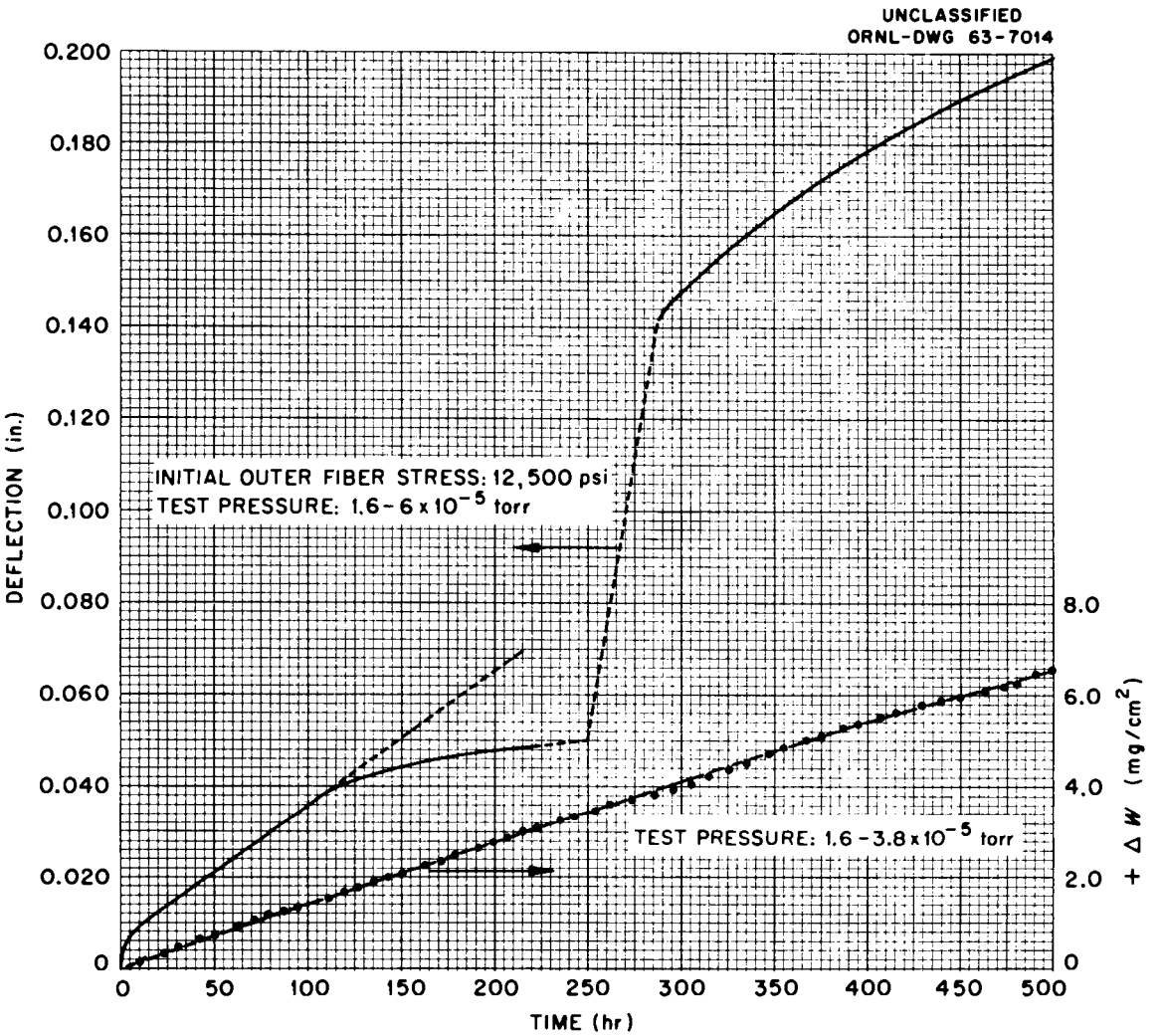


Fig. 8. Contamination and Deflection-Time Curves for Cb–0.6% Zr Tested at 1000°C in the 10^{-5} torr Pressure Range.

When oxygen contamination proceeded to the point where CbO precipitated, the alloy was weakened. It was possible to protect the specimen with a wrapping of molybdenum foil.

A precontamination treatment in the pressure range of 2.5 to 4×10^{-5} torr proved effective in strengthening the alloy during the early stages of test in this same pressure range.

During a single test, it was possible to alternately accelerate or decelerate the deflection rate of the alloy by systematically varying the pressure between the ranges of 10^{-5} and 10^{-7} torr.

Vacuums of better than 1×10^{-7} torr are required for minimizing the environmental effects observed for the test conditions described here.

ACKNOWLEDGMENTS

The author is grateful to H. Inouye, W. C. Thurber, and J. R. Weir for their comments on the presentation of the information contained in this report. Special thanks are due the following personnel for their contributions: J. F. Newsome, slow-bend testing; W. H. Farmer and R. S. Crouse, metallography; O. B. Cavin, x-ray diffraction; and W. R. Laing and staff, chemical analyses.

ORNL-3569
UC-25 — Metals, Ceramics, and Materials
TID-4500 (29th ed.)

INTERNAL DISTRIBUTION

1-3. Central Research Library
4. Reactor Division Library
5-6. ORNL — Y-12 Technical Library
Document Reference Section
7-26. Laboratory Records Department
27. Laboratory Records, ORNL R.C.
28. ORNL Patent Office
29. J. O. Betterton, Jr.
30. R. E. Clausing
31. R. S. Crouse
32. J. E. Cunningham
33. R. G. Donnelly
34. S. T. Ewing
35. J. H Frye, Jr.
36. R. G. Gilliland
37. G. Hallerman
38-42. M. R. Hill
43. H. Inouye
44. D. H. Jansen
45. C. E. Larson
46. A. P. Litman
47. T. S. Lundy
48. H. G. MacPherson
49. H. E. McCoy
50. C. S. Morgan
51-55. T. K. Roche
56. H. W. Savage
57. R. L. Stephenson
58. J. A. Swartout
59. W. C. Thurber
60. M. S. Wechsler
61. A. M. Weinberg
62. J. R. Weir
63. R. P. Wichner
64. A. A. Burr (consultant)
65. J. R. Johnson (consultant)
66. C. S. Smith (consultant)
67. R. Smoluchowski (consultant)

EXTERNAL DISTRIBUTION

68. C. M. Adams, Jr., MIT
69. G. M. Anderson, AEC, Washington
70. D. E. Baker, GE, Hanford
71. S. S. Christopher, AEC, Washington
72. T. D. Cooper, Wright-Patterson Air Force Base
73-74. D. F. Cope, ORO
75. E. M. Douthett, AEC, Washington
76. Ersel Evans, GE, Hanford
77. J. L. Gregg, Cornell University
78. R. Hall, Lewis Research Center
79-80. W. D. Manly, Union Carbide Corporation
81. T. M. McIntosh, AEC, Washington
82. W. McNeish, Universal-Cyclops
83. R. A. Noland, Argonne National Laboratory
84. R. G. Oehl, AEC, Washington
85. F. C. Schwenk, AEC, Washington
86. J. Simmons, AEC, Washington
87. E. E. Stansbury, University of Tennessee
88. D. K. Stevens, AEC, Washington
89. G. W. Wensch, AEC, Washington
90. M. J. Whitman, AEC, Washington
91. Research and Development Division, AEC, ORO
92-590. Given distribution as shown in TID-4500 (29th ed.) under Metals, Ceramics, and Materials category