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Report No. BMI-1243
C-25 Metallurgy and Ceramics
(M-3679, 20th Ed., Rev. 1)

UNCLASSIFIED

Contract No. W-7405-eng-92

DELTA-PHASE ZIRCONIUM HYDRIDE AS A SOLID MODERATOR

Classification cancelled (or changed to UNCLASSIFIED)
by authority of Ltr. Dr. Declassification Br. dated 2-11-59
by J. C. Ridenour TIE, date 2-13-59

by

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Action voided

~~Classification cancelled (or changed to SECRET)~~
~~by authority of Letter from Decl. Br. dated 1-31-58~~
~~by C. P. Boggess TIE, date 2-4-58~~

December 18, 1957

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DELTA-PHASE ZIRCONIUM HYDRIDE AS A SOLID MODERATOR

James B. Vetrano

In a study of the preparation and properties of delta-phase zirconium hydride it was found that large, sound bodies of the hydride can be prepared by direct combination of the elements if the rate of the reaction is retarded by limiting the supply of available hydrogen. Specimens up to 1-in. diameter were prepared using this technique.

Because delta-phase zirconium hydride does not readily form eutectics with iron- and nickel-base alloys below 1800 F these materials may be utilized for cladding the hydride. Delta-phase zirconium hydride is unaffected by exposure to liquid NaK or to nitrogen gas at temperatures below 1000 F.

The hot hardness of delta-phase zirconium hydride is about 130 kg per mm^2 *at room temperature and 40 kg per mm*^{2} *at 1500 F. The mean coefficient of thermal expansion (68 to 1337 F) is 6.5 x* 10^{-6} *per deg F. The thermal conductivity varies from 5.7 Btu/(ft)(hr)(F) at 300 F to 5.1 Btu/(ft)(hr)(F) at 1300 F.*

INTRODUCTION

Prior to this study it was known in a general way that delta-phase zirconium hydride is difficult to prepare in the massive form because it cracks and powders when the hydrogen is introduced and it cannot be recompacted to a high density. Furthermore, its brittleness at both room temperature and at elevated temperatures makes machining and hot working nearly impossible. With these difficulties overcome, however, it would make an excellent solid moderator since it has a high N_H. Since the delta phase is stable at all temperatures, thermal cycling should not result in dimensional changes associated with phase changes. The object of this study was to determine the properties of delta-phase zirconium and methods for its preparation so that it could be considered for use as a moderator material. Studies of the cladding of the hydride are reported in BMI-1244.

The zirconium-hydrogen phase diagram is shown in Figure 1(1). While four distinct single-phase regions are shown in this diagram, there is not complete agreement as to the distinction between the delta and epsilon phases. In this report, delta-phase zirconium hydride is defined as all material having a hydrogen-to-zirconium atomic ratio of between 1.5 and 2.0, or a N_H (number of hydrogen atoms x 10^{-22} per cm^3 of sample) between 5.5 and 7.3.

The chemical and physical properties of delta-phase zirconium hydride are found to be so markedly different from comparable properties of alpha- or beta-phase material at the same temperature that the composition dependence of these properties within the single delta-phase region is assumed to be negligible in comparison to temperature

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(1) References are at the end of the report.

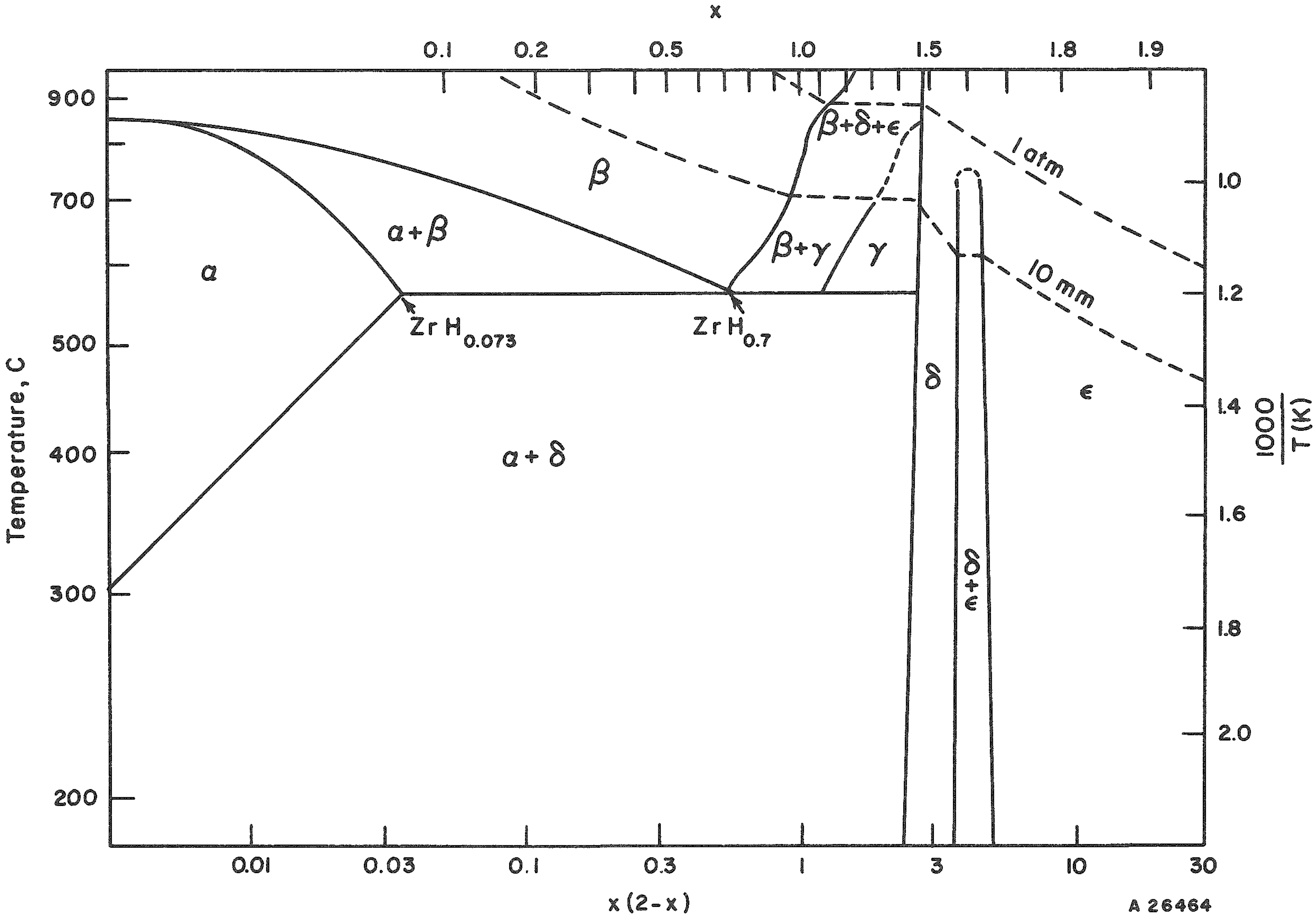

FIGURE 1. THE ZIRCONIUM-HYDROGEN SYSTEM, ACCORDING TO GILBERT(1)

x=H/Zr atomic ratio.

dependence. This assumption greatly simplifies the experimental measurements since it is possible to maintain a constant composition of hydride over a temperature range only by continually rebalancing the surrounding hydrogen pressure. Possibly with refinement of the experimental techniques one could show some composition dependence of quantities such as thermal expansion, thermal conductivity, or hardness within the single delta-phase region.

PREPARATION OF THE HYDRIDE

Delta-phase zirconium hydride is quite readily prepared by direct combination of the elements at elevated temperatures. However, since the process involves a crystalline rearrangement from hexagonal close packed to face-centered tetragonal with an accompanying density change from 6.5 to about 5.5 g per cm^3, the material is subjected to severe internal stressing during the hydriding process. Since delta-phase hydride is relatively brittle this stress is relieved by fracturing. This difficulty can be largely overcome by carefully controlling the rate of hydriding so that the transformation from the ductile beta-phase hydride to the brittle delta-phase hydride occurs so slowly that steep hydrogen-concentration gradients are never established in the specimen.

Using 1/4-in.-diameter by 1-in.-long specimens it was found possible to prepare uncracked beta-phase hydride at 1500 to 1700 F in less than 1/2 hr because of the rapid rate of diffusion of hydrogen in beta zirconium in this temperature range. Standardizing on a time of 2 hr for this step (to insure complete annealing of the specimens), the rate of hydriding through the beta-delta two-phase region at about 1500 F was varied. It was possible to prepare uncracked delta-phase hydride specimens only if the time for this transformation was at least 4 hr. Using 1/2-in.-diameter by 1-in.-long specimens 4 hr was insufficient. It was necessary to allow at least 20 hr for this second stage of hydriding to obtain uncracked specimens 1/2 in. in diameter. The hydriding time required for maintaining homogenization of the specimen through the phase transformation (and consequently avoiding cracking) is therefore found to be roughly proportional to the square of the diameter. Applying this rule to 1-in.-diameter by 3-in.-long specimens it was found that sound specimens were produced by hydriding through the two-phase region at a uniform rate for 60 hr (Figure 2) while cracked specimens resulted with a 7-hr test.

Table 1 gives the optimum times, as determined in this study, for hydriding cylinders of zirconium hydride from $ZrH_{1.0}$ to $ZrH_{1.5}$ at 1500 F and the corresponding uniform rate of hydrogen addition. The zirconium is initially hydrided to $ZrH_{1.0}$ at 1500 to 1700 F over a period of about 2 hr.

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FIGURE 2. SLOWLY HYDRIDED ZIRCONIUM CYLINDERS ($N_H = 6.2$)

1-in.-diameter by 3-in.-long cylinders of delta-phase zirconium hydride ($N_H = 6.2$) prepared by hydriding at a uniform rate for 60 hr through the beta-delta two-phase region at 1500 F.

TABLE 1. OPTIMUM HYDRIDING TIMES FOR PREPARING DENSE DELTA-PHASE ZIRCONIUM HYDRIDE FROM BETA-PHASE ZIRCONIUM HYDRIDE AT 1500 F

Cylinder Diameter, in.	Rate of Hydrogen Addition, cm^3 (STP)/(g Zr)/(hr)	Reaction Time, hr
1/4	2.46	4
1/2	0.492	20
1	0.164	60

The specimens are brought to their final composition while cooling at a controlled rate in a deficiency of hydrogen. The maximum allowable cooling rate was not definitely established, but 100 F per hr down to 600 F was found to be slow enough for 1/4-in.-diameter specimens, and 25 F per hr down to 600 F was found to be slow enough for 1/2- and 1-in.-diameter specimens.

Surface preparation of the samples prior to hydriding is very important since oxide, nitride, or grease films will inhibit hydriding. The standard pretreatment adopted for this study was to lightly abrade the specimens with 120-grit aluminum oxide paper after they had been machined to the proper dimensions. They were then degreased in hexane.

The hydrogen used in this study was purified by passing it successively through a Deoxo catalyst purifier, a heated bed of calcium hydride, and finally through a cold trap maintained at the boiling point of liquid nitrogen.

CHEMICAL PROPERTIES OF THE HYDRIDE

The compatibility of delta-phase zirconium hydride with various metallic materials was determined. For those metallic materials which were available in rod form, cups having a 1/2-in.-diameter cavity with a flat bottom were machined and the cavity filled with hydride. A cap of the same material as the cup was then pressed in place and welded tight. For those materials available only in sheet form the cups were made of AISI Type 303 stainless steel and the cavity filled with hydride sandwiched between disks of the material to be tested. The welded elements were heated at 1700 F for 1 week in graphite dies in a flowing argon atmosphere under a dead load of about 2000 to 3000 psi. The load was applied by means of an external lever-arm device and transmitted to the elements by means of graphite plungers.

Evaluation of the compatibility was made by sectioning the cooled cups and examining the hydride boundary metallographically for diffusion zones. The least diffusion was noted with chromium, AISI Type 446 stainless steel, niobium, and molybdenum, while nickel, Nichrome, Nichrome V, Inconel, Armco, and AISI Types 303 and 347 exhibited intermediate diffusion, and copper attacked the hydride severely.

Comparison tests made with beta-phase zirconium hydride showed that it acted like zirconium metal; for example, forming intermetallics with nickel and Nichrome V at 1700 F. The delta hydride, on the other hand was stabilized by its higher hydrogen concentration.

Specimens of delta-phase zirconium hydride were exposed to nitrogen at temperatures of 1000 to 1500 F and pressures of 1 to 13 atm for about a week. The resulting corrosion was determined by weight gain, metallographic analysis, and chemical analysis for nitrogen. At 1000 F the delta-phase zirconium hydride was scarcely affected by the treatment, and at 1500 F the depth of the nitride scale formed was only about 0.15 mil.

The compatibility of delta-phase zirconium hydride with liquid NaK was determined by two essentially different techniques. One involved heating a specimen of hydride in a NaK-filled capsule of Type 304 stainless steel for about 120 hr at a constant temperature. The other involved intermittently washing NaK of a certain temperature over the specimen maintained at a temperature of 300 to 700 F lower than the NaK. This was accomplished by holding the specimen restrained in one end of a capsule partially filled with NaK and rocking the capsule. The ends of the capsule were independently heated by resistance wire-wound furnaces to the desired temperatures. The extent of the corrosion was determined from dimensional changes of the specimens, and from inspection of the surfaces for changes in color and appearance of premachined grooves.

The results of the experiments using both techniques indicated that below 1000 F there is essentially no corrosion of delta-phase zirconium hydride by NaK. Above this temperature, there is increasing corrosion, manifesting itself in the formation of unidentified brown or black surface films.

PHYSICAL PROPERTIES OF THE HYDRIDE

The hot hardness of delta-phase zirconium hydride was measured up to 1500 F. The apparatus used consisted essentially of a Vickers-type sapphire indenter enclosed in a sealed chamber. The sample could be manipulated remotely within the chamber through a screw-drive mechanism, and repositioned after each measurement. In this manner it was possible to make several impressions on the same sample without cooling the apparatus and opening the chamber. While the specimen was being heated, the chamber was continuously flushed with a hydrogen-helium mixture at atmospheric pressure. The proportion of hydrogen in the gas mixture was chosen so that it would be equivalent to the dissociation pressure of the particular specimen at the temperature of measurement. This was done to avoid changes in composition of the condensed phase during the measurements. Since premixed gases were used, it was possible to make measurements at only one temperature for each specimen. Some room-temperature measurements were made on a standard Tukon hardness tester.

The results of all of these measurements are given in Table 2. No abrupt softening of the material was observed up to the temperature limits of the tests.

The thermal conductivity of delta-phase zirconium hydride was determined by a steady-state heat-flow method, using nickel-plated specimen disks 0.2 in. thick and 0.787 in. in diameter. Good contact between the specimen and the heat reservoir and sink was assured by tinning the specimens to the Armco iron standard rods which conducted the heat to and from the specimens. All measurements were made in a flowing stream of hydrogen at 1 atm pressure. The apparatus is shown schematically in Figure 3.

Table 3 shows interpolated thermal-conductivity values taken from a best curve drawn through the five experimental points. It is estimated that these values are not in error by more than 10 per cent.

TABLE 2. HOT HARDNESS OF DELTA-PHASE ZIRCONIUM HYDRIDE

Composition	Temperature, F	Atmosphere, volume per cent	Hardness, kg per mm^2	Apparatus
$ZrH_{1.60}$	Room	100 air	164	Tukon
$ZrH_{1.60}$	Room	100 air	209	Vickers
$ZrH_{1.90}$	Room	100 air	128	Tukon
$ZrH_{1.90}$	Room	100 air	126	Vickers
$ZrH_{1.93}$	1020	100H	46.7	Vickers
$ZrH_{1.88}$	1031	10H-90He	49.2	Vickers
$ZrH_{1.88}$	1148	100H	54.5	Vickers
$ZrH_{1.60}$	1310	10H-90He	46.5	Vickers
$ZrH_{1.60}$	1490	100H	42.5	Vickers
$ZrH_{0.80}$(a)	1508	10H-90He	8.7	Vickers

(a) Beta-phase zirconium hydride comparison test.

TABLE 3. THERMAL CONDUCTIVITY OF $ZrH_{1.63}$

Temperature, F	Thermal Conductivity, Btu/(hr)(ft)(F)
300	5.7
500	5.6
700	5.4
900	5.3
1100	5.2
1300	5.1

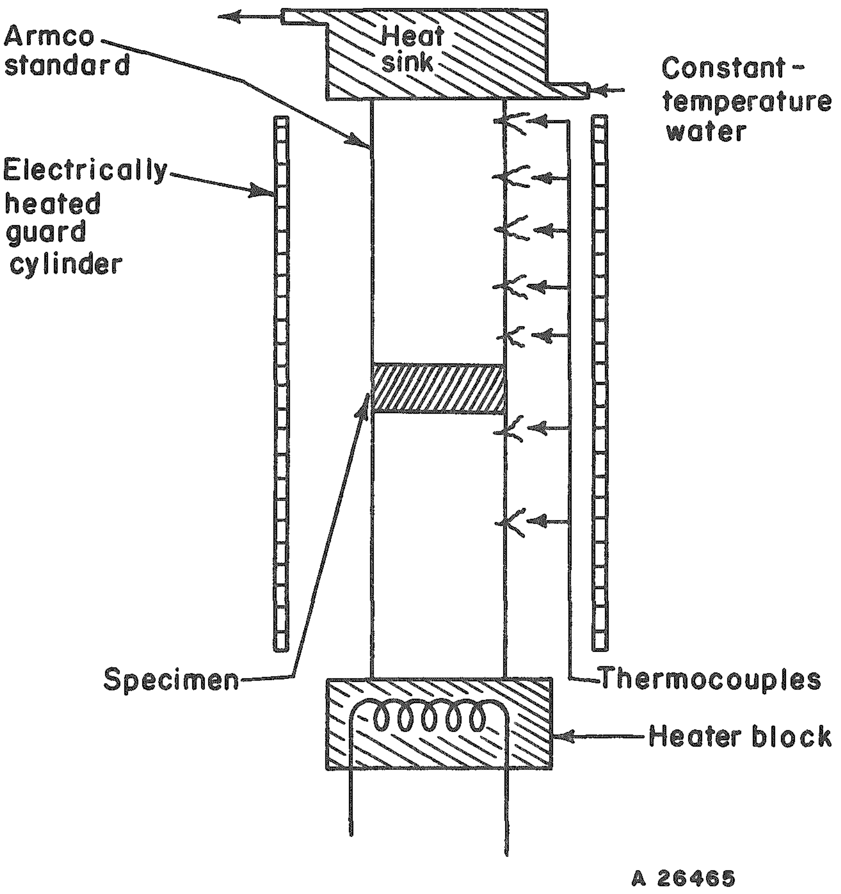

FIGURE 3. SCHEMATIC DRAWING OF THE APPARATUS USED TO MEASURE THERMAL CONDUCTIVITY OF DELTA-PHASE ZIRCONIUM HYDRIDE UP TO 1500 F

The linear thermal expansion of delta-phase zirconium hydride was measured up to 1500 F. The sensing element of the dilatometer employed was a motor-driven micrometer. The micrometer was continuously driven toward the lever mechanism, which was actuated by the expanding sample, until it made contact with the lever mechanism. The motor drive was then automatically reversed for a small time interval and the cycle repeated. The movements of the micrometer screw and the specimen temperature were automatically recorded.

A 1/4-in.-diameter by 3-in.-long specimen of $ZrH_{1.82}$ was used for the measurements. It was heated at a rate of 5.4 F per min while the dilatometer was being continuously flushed with a 50-50 mixture of hydrogen and helium. Measurements were made both during the heating and the cooling cycles for two consecutive runs. The expansion curves for the two heating cycles were averaged and the averaged values adjusted to read zero at 68 F. These adjusted values are plotted in Figure 4. Figure 4 also contains, for comparison, some unpublished data for two types of stainless steel and for molybdenum.

A limited investigation was undertaken to confirm the existing dissociation-pressure data in the delta-phase up to 1 atm of pressure. The experimental data obtained were fitted by means of the least-squares method to the following equation:

$$\log P = 6.207 + 3.095 \log \frac{C}{2.00\ C} - \frac{8741}{T} ,$$

where

P = pressure, atm

C = composition of the hydride, g-atoms of hydrogen per g-atom of zirconium

T = temperature, K.

Using this formula the pressure versus reciprocal-temperature curves were plotted for several isochores. These are shown in Figure 5. The graph also shows the isochores determined by Gilbert(2). Excellent agreement between this work and Gilbert's is evident at a 1-atm pressure and in the range of $ZrH_{1.5-1.7}$, but at lower pressures and higher hydrogen concentrations the deviations become pronounced.

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(1) Gilbert, Paul T., Jr., "Zirconium Hydride - A Compendium on the Systems Zirconium-Hydrogen and Hafnium-Hydrogen and Related Topics", NAA-SR-1508 (Oct. 15, 1956). Secret.

(2) Gilbert, Paul T., Jr., and Goeddel, Walter V., "Zirconium Hydride: Part I. Dissociation Pressure; Part II. Radiation Stability", NAA-SR-1399 (Apr. 15, 1956). Secret.

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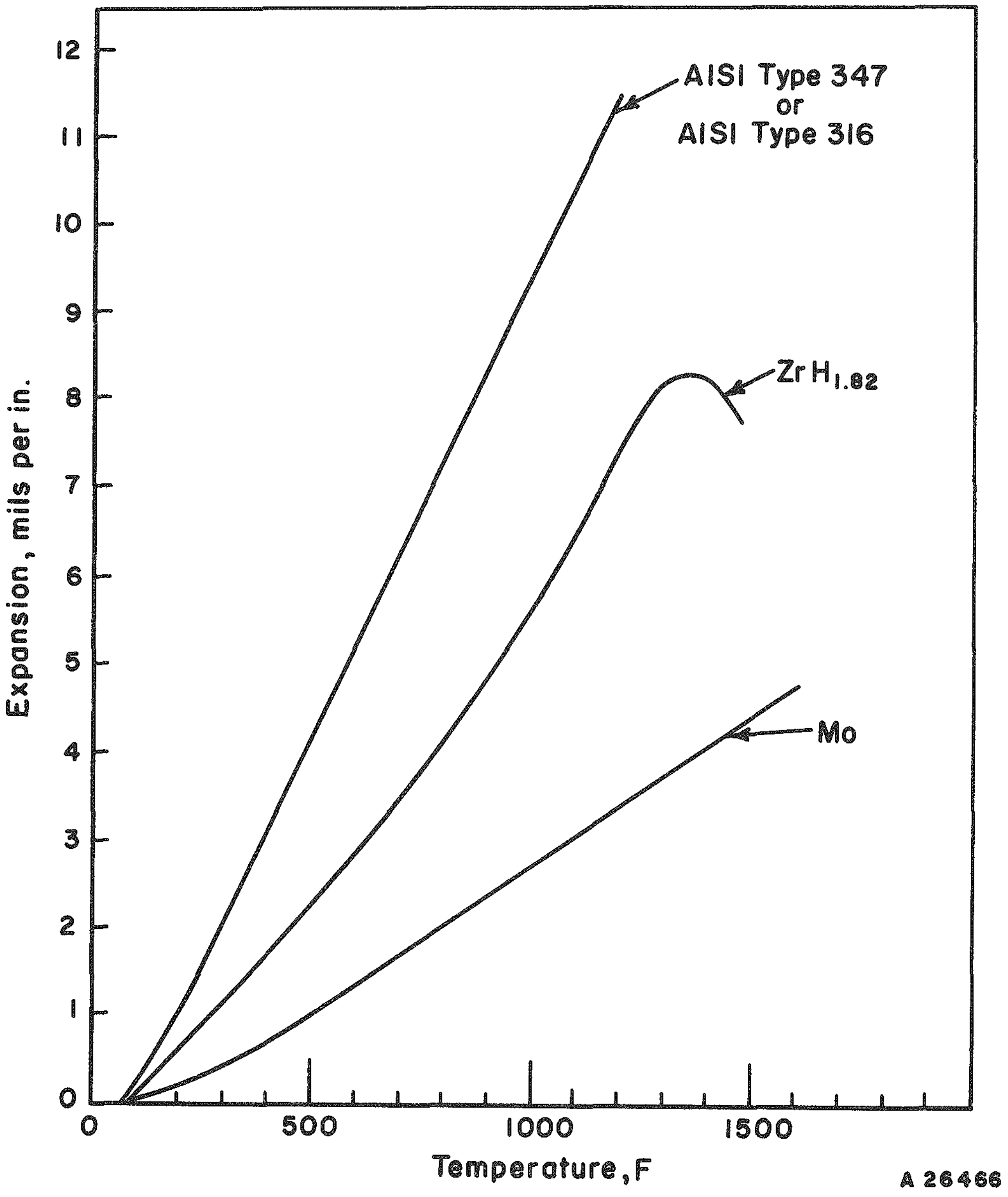

FIGURE 4. EXPANSION OF $ZrH_{1.82}$ COMPARED WITH MOLYBDENUM AND TWO STAINLESS STEELS

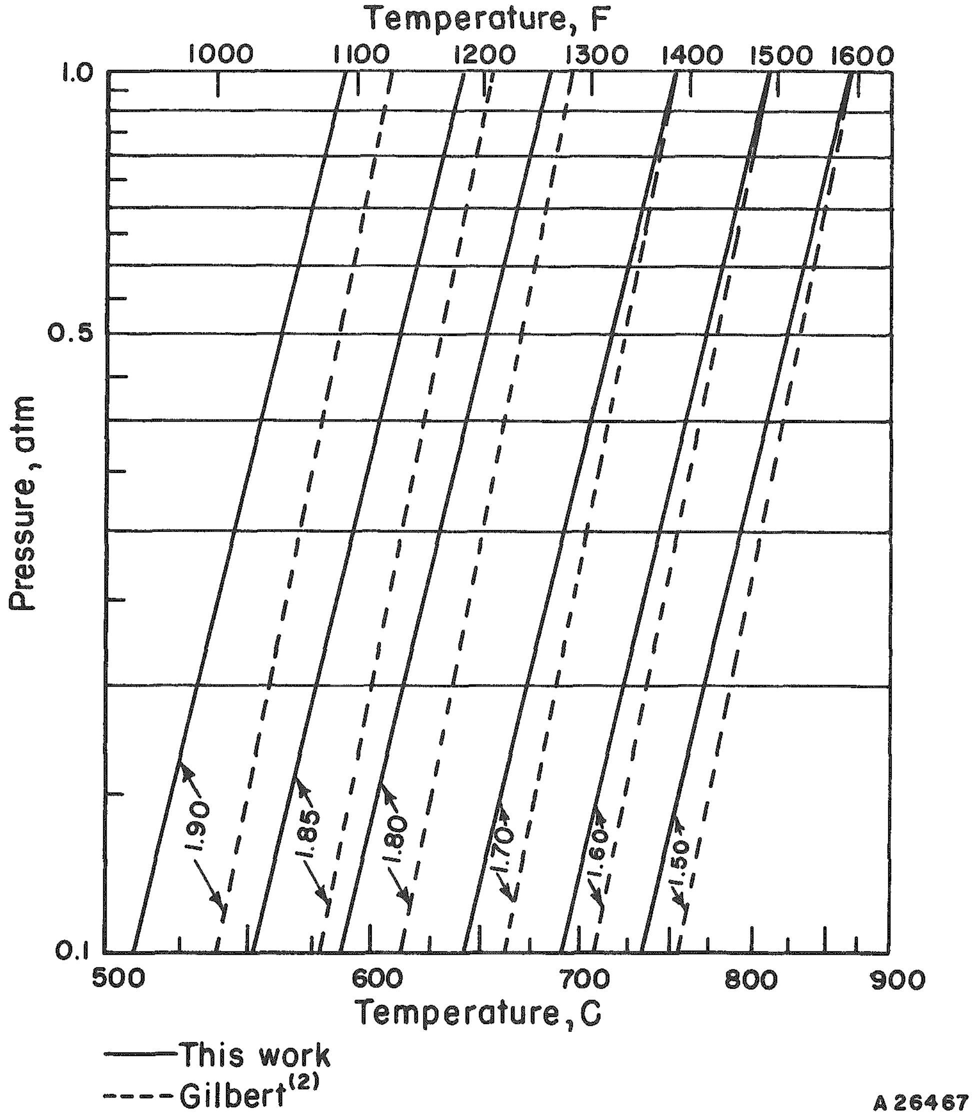

FIGURE 5. PRESSURE VERSUS TEMPERATURE FOR VARIOUS HYDROGEN-TO-ZIRCONIUM ATOMIC RATIOS