LOW AND HIGH TEMPERATURE MECHANICAL PROPERTIES OF ANNEALED ZIRCONIUM

by

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A brief history of the metal is in order since the final properties of the pure metal depend upon the method of forming, the amount of cold working, annealing temperatures, etc. The pure ingot was No. 74, obtained from the United States Bureau of Mines in the summer of 1948, and contained 0.013 per cent iron and 0.247 per cent carbon by weight. The metal was cast into a $2\frac{1}{2}$ inch diameter mold, after having been prepared by the Bureau's process of reducing zirconium chloride with molten magnesium. The metal was covered with Shelby tubing and forged to a 6 in. x 6 in. x 1 in. slab. It was then cut into strips and annealed at 1200 F before swaging. The swaging dies were changed in fifty thousandths increments, and the final rod was reduced to 0.530 in. diameter. Some of the hard scale was then removed with a file in order to examine the rod for swaging defects. The cross section of the strips before swaging was approximately one inch square. The yield was twenty-one 0.351 inch diameter specimens, each $3\frac{1}{2}$ inches long, and two 0.351 inch diameter specimens 11 inches long. After machining, the specimens were all annealed at the Bureau Laboratory. Since the metal was relatively new and scarce, some notes were taken on the cutting and machining properties of the metal, and these can be found in the appendix of this thesis. The annealing before testing was done at 700 C in a helium atmosphere for one hour.

CONSTRUCTION OF EQUIPMENT

The instruments specially constructed consisted of an extensometer, a stress-strain recording drum, a high temperature tensile furnace, and a hardness furnace. The first job involved reworking a commercial laboratory furnace of 1800 watts capacity to meet the following requirements: Sufficient capacity to permit temperatures of 1200 F or higher; sufficient sensitivity to give accurate control; proper design to prevent natural chimney effects and consequent unequal temperature distribution; openings for extensometer arms, thermocouples, and holders. Auxiliary heating elements of 750 watts capacity were attached to the top and bottom of the furnace surrounding the holders. These coils and the main furnace element were all three separately controlled by Variac transformers.

The construction of the extensometer called for making an instrument that would withstand the rigors of high temperatures, that would meet the requirements for accuracy, and that could be conveniently read outside of the furnace. The final design can best be seen by inspection of the photograph of the equipment, Figure 1. Carboloy tips were peened into small screwed studs set into the rings to form the pivot points. Of course, all parts of the extensometer

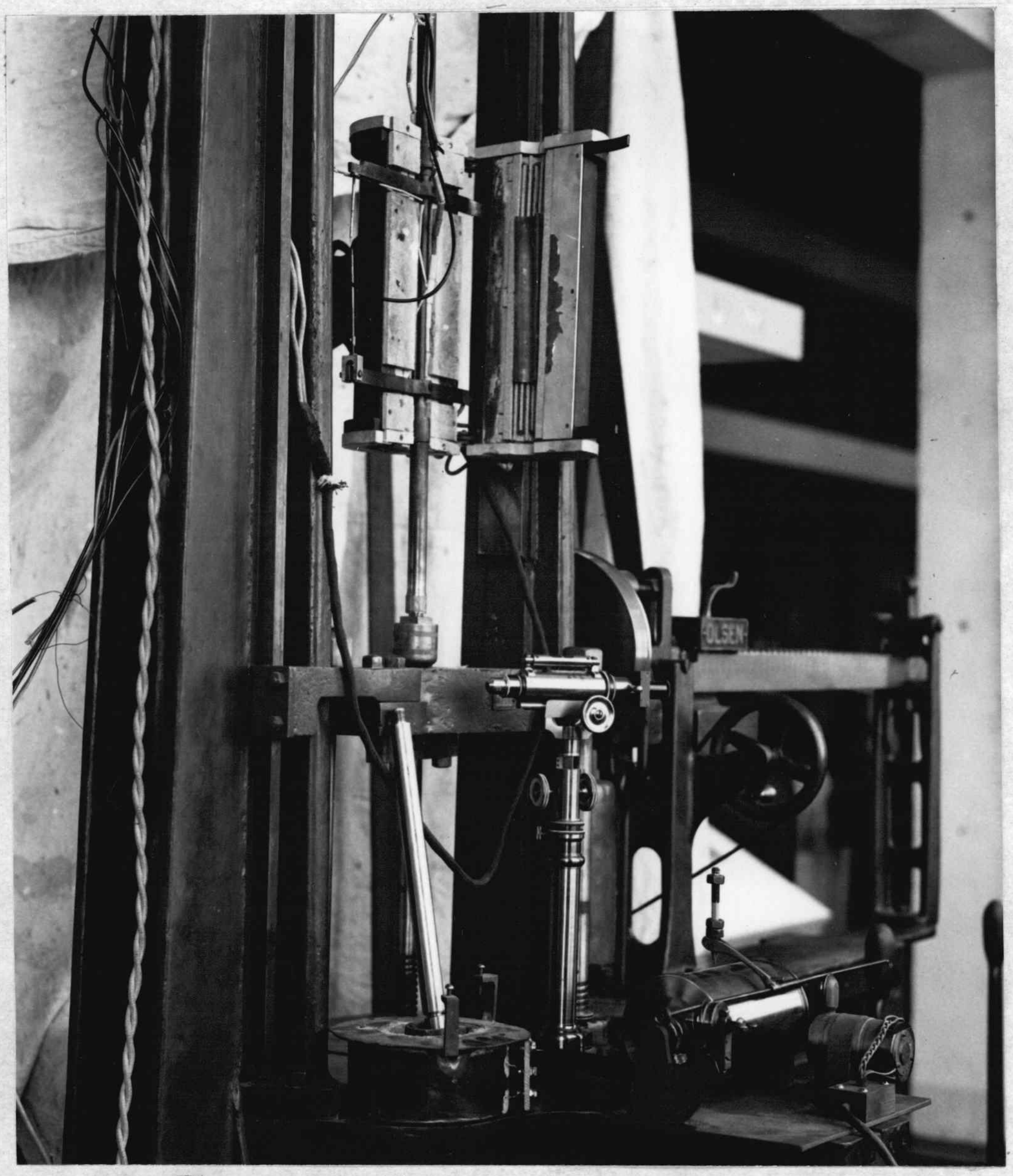

Figure 1. Photograph of Equipment.

Shows extensometer, furnace, and Inconel sleeve in the furnace. Telescope, hardness equipment, and stress-strain recorder alongside.

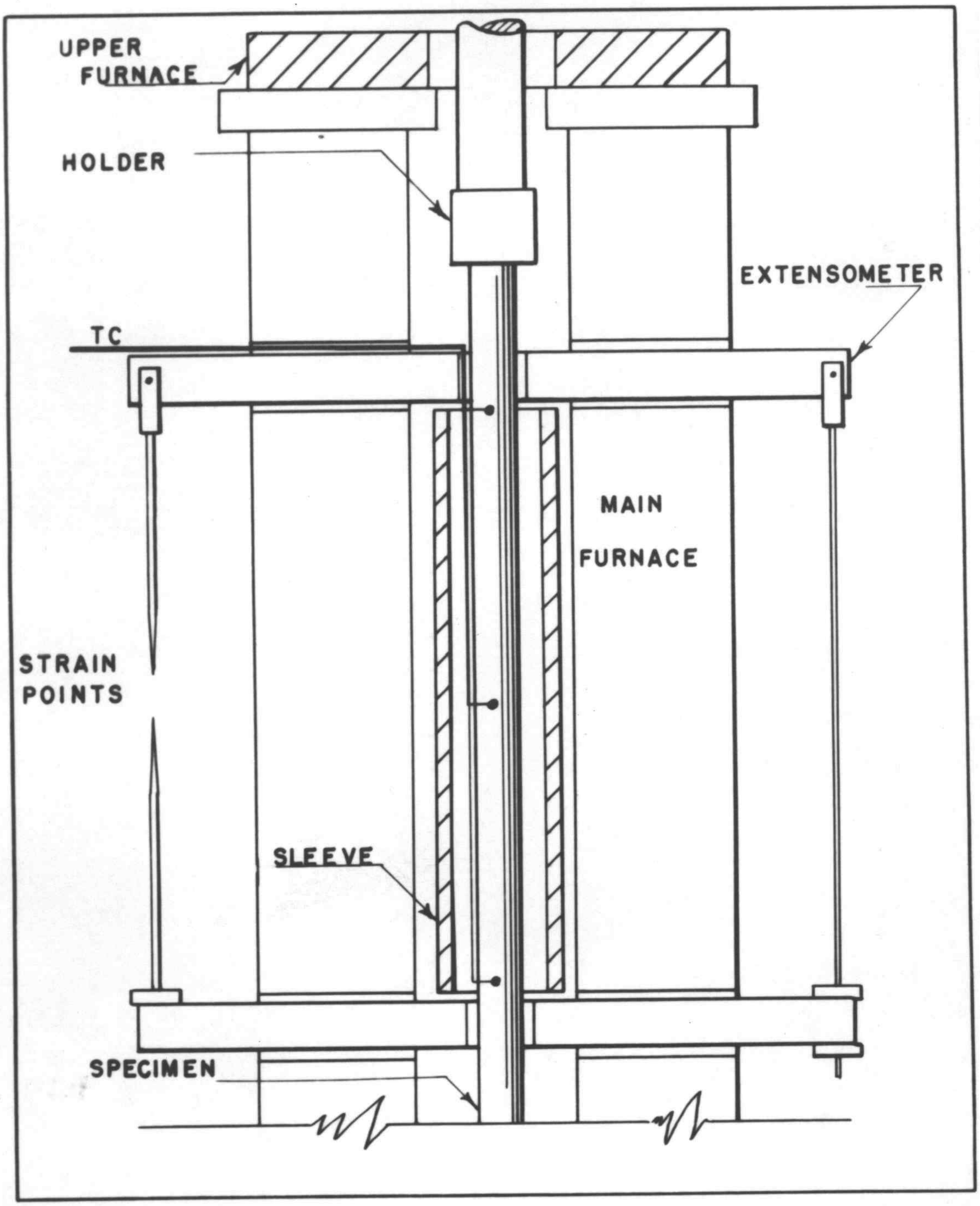

FIGURE 2 MODULUS OF ELASTICITY APPARATUS

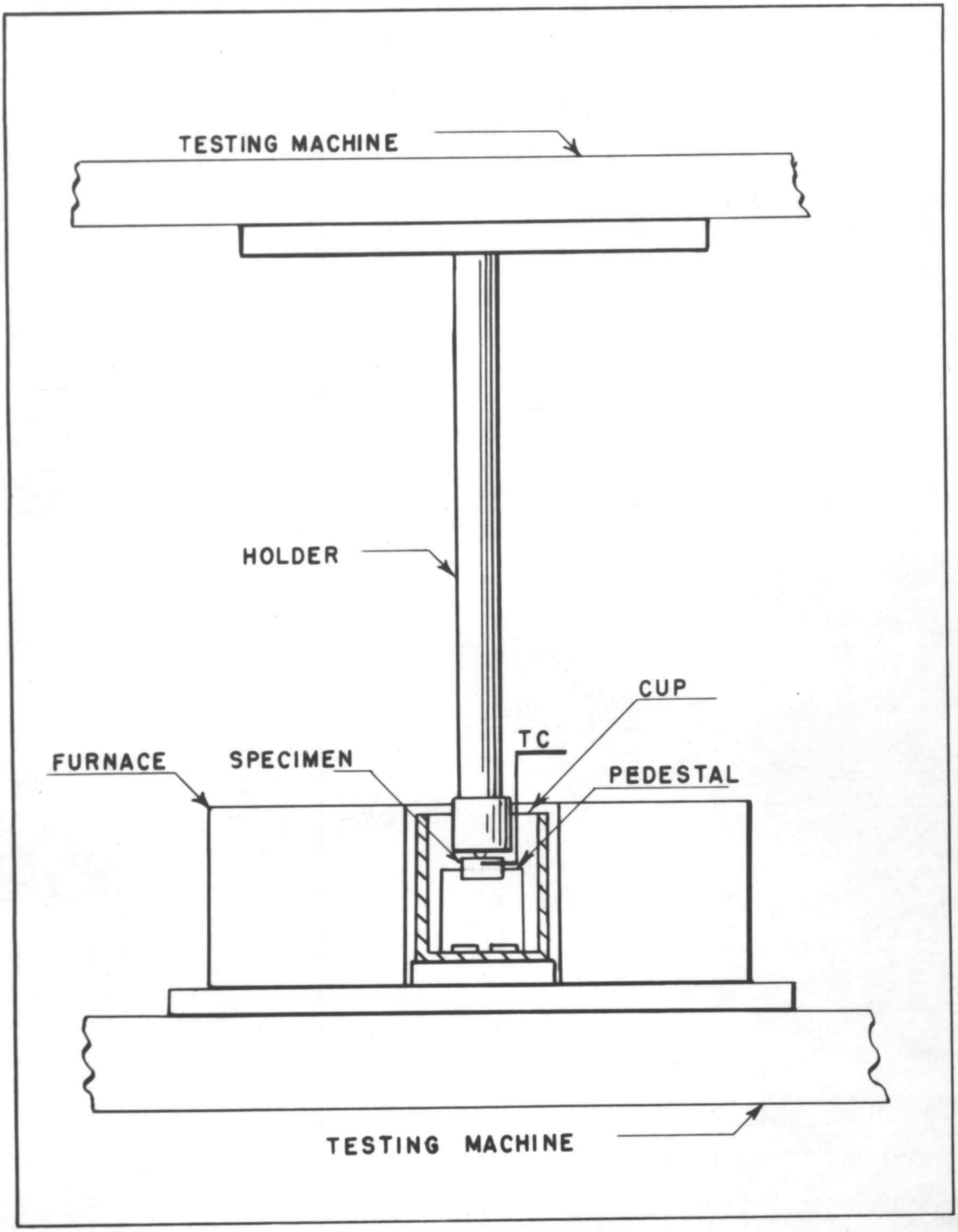

FIGURE 3 HARDNESS TESTING APPARATUS

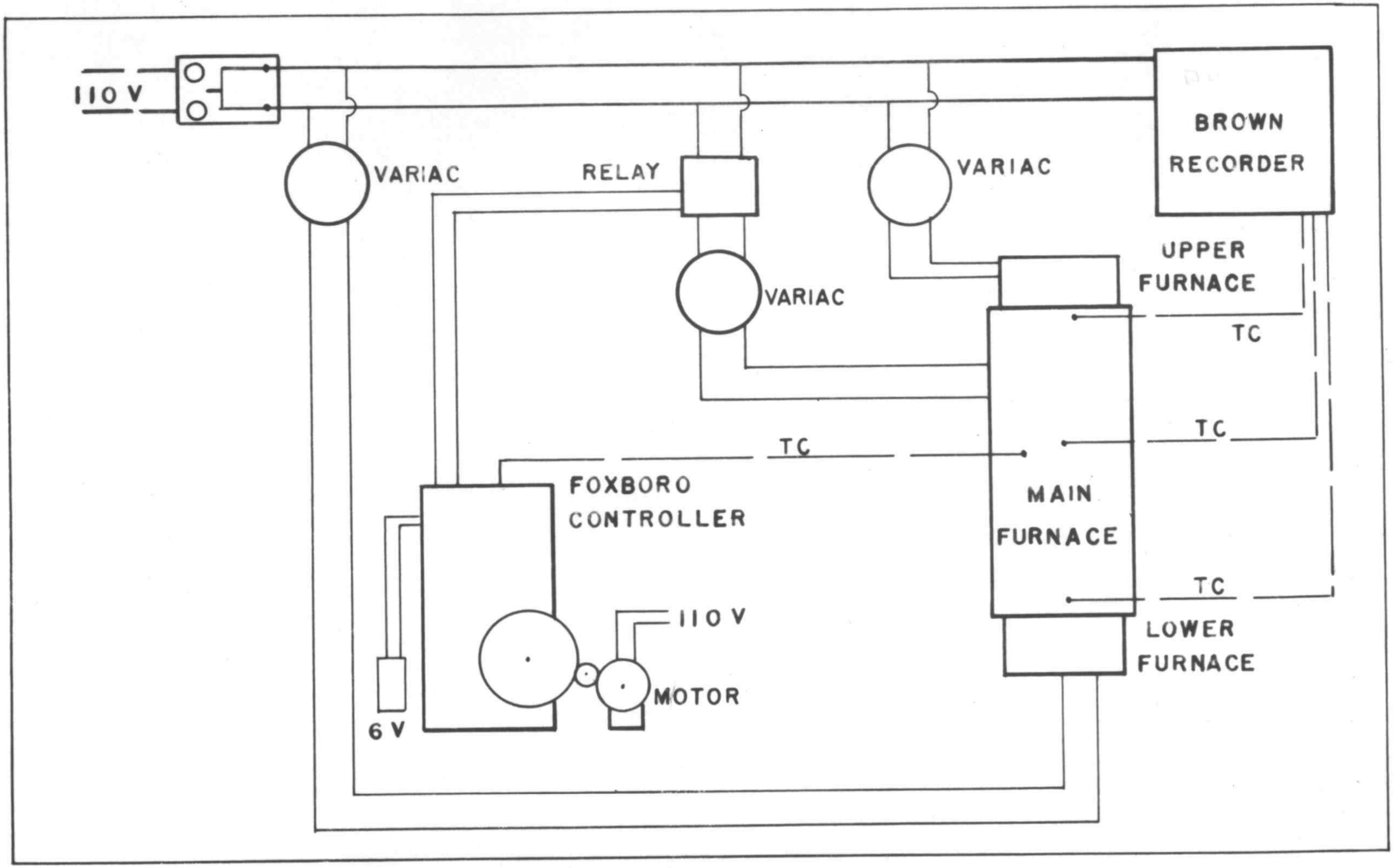

FIGURE 4 DIAGRAM OF INSTRUMENT PANEL

were not at the same temperature during running of the test, but since the strain measuring points could be adjusted anytime, it was only necessary to wait until thermal equilibrium had been established and then set the points for a zero reference.

The stress-strain recorder was made from a three inch brass cylinder, mounted in ball bearings, and gear reduced to give the proper load scale of 1 inch equals 10,000 lb. The purpose of the recorder was threefold: To obtain the breaking strength; to obtain the ultimate tensile strength; and by use of the offset method to get the yield point. Success of the last purpose was not fulfilled. The yield point was not definite enough to obtain a sharp knee in the curve or sudden drop of the beam, and with a one inch gage length the offset method of obtaining yield point was impractical. The ordinate on the graph was stress or load and the motion was transferred from the rotating load dial via selsyn instruments to the brass drum. The abscissa or horizontal motion was obtained from the moving head of the testing machine, and was conducted to the recorder pencil by steel piano wire running over brass pulleys.

The hardness testing equipment consisted of a furnace, a specimen pedestal, and a holder for a 1/8 inch Carboloy ball. An electric furnace was built to contain a steel cup, which in turn was to hold a pedestal. See Figure 3. The pedestal had to be drilled and tapped to receive the hardness specimen to prevent its floating around in the molten tin during the high temperature tests. The ball holder was made from a piece of Inconel 12 inches long.

Inconel holders were also machined for the high temperature tensile tests since the specimens were only $3\frac{1}{2}$ inches long and the main furnace and auxiliary furnaces had an overall length of 20 inches.

INSTRUMENTS USED

Tinius Olsen 30,000 beam balance testing machine

Foxboro potentiometer controller

Brown Electronik recorder

Leeds and Northrup potentiometer No. 538885

Ernst Leitz measuring microscope

Variac transformers

Mercoid relay

Stress-strain recorder

Furnaces, extensometers, specimen holders

The Foxboro potentiometer type control pyrometer and the Brown Electronik recorder both were equipped with an automatic cold junction compensator. The Brown instrument was equipped to record four thermocouple readings, and cycles every thirty seconds. Each roll of recording graph paper is 45 feet long, and with one inch representing 15 minutes of operating time, a total of 135 hours of actual temperature recording is available on each roll. One complete roll was used for the tensile tests and the modulus tests alone. This particular recorder was designed to be used with chromel-alumel thermocouples, and although these thermocouples are not suitable for the low temperature work, they are very satisfactory for temperatures up to 2000 F. The Leeds and Northrup potentiometer was a very precise instrument for measuring the extremely low temperatures, and was calibrated with an iron-constantan thermocouple.

PREPARATION FOR THE TESTS

The zirconium slab was furnished by the Bureau Laboratory, but all of the cutting, swaging, filing, and machining was done by the author to get the desired number and size of specimens.

The furnace survey was conducted first according to ASTM specifications for high temperature work in order to give some idea of uniformity of temperature distribution, and thus some basis for judgment of reliability of the results. A steel dummy specimen was prepared--an exact replica of the zirconium specimens. The dummy was drilled at the prescribed locations and the thermocouples were inserted and set in place with high temperature cement. Several high temperatures were then tested, and the variation noted along the specimen. Without the two auxiliary furnaces at top and bottom the temperature variation was very large. Addition of the two furnaces permitted easy adjustment to obtain equal temperatures along the whole specimen. Proper sealing of all cracks and openings was vitally necessary to hold down large fluctuations in the thermocouple readings. After the survey was completed, twelve steel specimens were broken under actual test conditions in order to discover any difficulties and to check the best testing procedure. After being satisfied on these points, the actual zirconium tests were started. All necessary measurements of each specimen were taken, one inch gage marks were set off, and the speed of loading was set at 0.04 inches per minute. Three thermocouples were connected to each specimen--one each to the top and bottom, and one to the middle which served both as a recorded temperature and as a control thermocouple going to the Foxboro instrument. A double-pole double-throw switch served to connect the middle thermocouple either to record or control. A Mercoid relay was used as an actuator for the less than one ampere exciter current from the controller as a means of closing the main furnace line voltage. A Variac transformer was connected to each furnace, and gave a very delicate selection of line voltages as an aid in getting just the right current for each temperature tested. The Foxboro controller was set up and a motor and reducing device attached to cycle the depressor bar every six seconds. The stress-strain instrument was checked for play and alignment; the thermocouples were wrapped with asbestos cord; the Inconel equalizer sleeve was attached, and the furnace was closed and sealed ready for testing.

The ultimate tensile tests at the low temperatures presented a somewhat different problem in that some liquid bath had to surround the specimen completely to give a good uniform temperature. A bath of gasoline and dry ice was selected for this medium--gasoline for several reasons: It was inexpensive, readily available, and has a very low freezing point. With this combination, temperatures down almost to the freezing point of CO_2 were achieved. The equipment to handle this combination consisted of two metal cylinders, one inside the other, with rock-wool separating the two. Neoprene packing nuts were used to prevent leakage around the specimen holders where they emerged from the can. About a pound and a half of dry ice was required to lower the temperature of the gasoline, equipment, and specimen for each test. Several specimens were broken at the low temperatures.

Preparing for the modulus of elasticity tests involved accurately locating 8-inch gage marks for the extensometer, getting the pivot points firmly set in the marks, and carefully setting the whole assembly into the furnace. After this operation, thermocouple wires were led down through the openings and securely tied to the top, bottom, and middle. The adjusting thumb screws on the vertical rod helped to parallel the extensometer arms, and further adjustment of the strain points brought them to within a millimeter of each other ready for reading. Final snug adjustment of the Carboloy pivot points and insertion of the Inconel sleeve about completed the preparations. The extensometer had to be checked frequently for freedom of motion and freedom from excessive friction.

The most difficult problem in the low temperature work, was in obtaining uniform temperature for the modulus of elasticity tests. Several possibilities were considered such as surrounding the whole specimen with brine tubes, circulation of cold air, or dripping in liquid air. The method finally used was a canvas sack wrapped around the specimen over its full length and packed with finely chipped dry ice. The temperature distribution was not very even, but a reasonably representative mean temperature could be calculated from the three thermocouple readings. For this test, the Leeds and Northrup potentiometer was used with the three thermocouples hooked up to three separate switches so that each thermocouple could be connected to the instrument in turn. This gave a continuous reading on all three thermocouples every 20-30 seconds.

Preparing for the hardness tests at the high temperatures concerned the machining, grinding, and polishing of the test surfaces, plus the drilling of a small hole in the side of the specimen just 1/8 of an inch below the surface for insertion of the thermocouple. Since the test specimens were so small, the standard Brinell test ball of 10 mm diameter would be too large for so small a surface. Decision to use the Brinell method was made because it would be easier to make a holder to apply a measured load on the Olsen testing machine than to provide a non-yielding base for a Rockwell test. Since hardness measured with any ball other than a Brinell 10 mm ball is not considered a standard test, some assurance of a reasonable relation to a standard test had to be forthcoming to make the hardness test made with the smaller ball valid. The 1/8-inch ball was therefore calibrated against a standard Brinell ball. This was done by making several indentations in eight different pieces of material with both balls, and by then calculating hardness for both indentations by the formula $H = \dfrac{P}{\frac{\pi D}{2}\left(D - \sqrt{D^2 - d^2}\right)}$. P is the load, D is the ball diameter, and d is the diameter of the indentation. P is obtained from the accepted formula $P = 5D^2$. For a 1/8-inch ball this formula gives a load of 50.5 kilograms or

111.1 pounds. Both ball indentations were then measured, hardness was calculated, and the results were plotted one as ordinate and the other as abscissa. The tests covered a wide range of hardness, and very close agreement between the two methods was observed. With the equipment then set in place, the hardness tests were started.

TESTING PROCEDURE

The tensile specimens were brought up to temperature within 30 to 60 minutes and held there for nearly one hour before breaking. After cooling, the specimens were removed and the gage marks were measured for calculation of elongation. The specimen was then stamped with numbered dies to correspond with the temperature at which it was broken. The tensile strength was then plotted immediately for each temperature. One specimen was broken every 100 F until 1200 F was reached in order to establish the trend of the curve. Check points were then made at those temperatures that seemed a little off the trend path, and it is seen that extra specimens were broken at -100 F, 300 F, and 600 F.

For the modulus of elasticity tests it was necessary to check for the establishment of thermal equilibrium before starting the tests. This was done by setting the points at some reference dimension, and then by checking them every few minutes with the microscope to make certain they had not changed. The points were then finally adjusted and several cycles of loading and unloading were applied to set the points and to take out most of the excess play in the grips, holders, screws, etc. Starting with an initial load of 50 lb, the specimen was loaded in 100 lb increments to within 75 per cent of the expected yield point. Each strain reading was read to the smallest division of 45 millionths of an inch. The strain for each 100 lb load increment varied from about 0.0009 inches at the lower temperatures to 0.0020 inches at the higher temperatures. The instrument could have been read so that the smallest division was 9 millionths of an inch, but the large variation between readings did not indicate that such sensitivity was warranted. After loading to the maximum for that temperature, the load was gradually released to the original 50 lb and the points were checked for returning to the zero reference. From five to twelve loading cycles were made at each temperature. This gave from fifteen to forty strain readings to average for the run. At any rate, strain readings were taken until the consistency of the data and their reasonableness seemed to indicate that the equipment was functioning properly. During each run a constant check was kept on the recorder to see that strain readings were not taken during a period of great fluctuation in the thermocouple readings. A table of the auxiliary voltages was kept so that at each new temperature the proper increase in the auxiliary furnace voltage could be made to give good agreement on all three temperatures. The chart record bears out the remarkable agreement that did exist at even the higher temperatures with all three thermocouples.

The testing procedure for the hardness tests was most simple. Glycerine was used below 450 F to submerse the specimen, but above that temperature it caught fire and molten tin was used. As soon as the liquid and specimen reached the correct temperature, the holder was carefully lowered just to the surface of the specimen. The load was slowly applied, taking 60 seconds to do so. The longer time was used instead of the usual 30 seconds, because of the longer time required to apply the load than for the standard Brinell test. Two or three indentations were made in each specimen, and the diameter of each indentation was checked immediately to see if further tests on that specimen were necessary. In some cases of doubt, both sides of the specimen were used for the tests, and several readings were taken of each indentation. The top of the liquid was at least a quarter or half of an inch above the surface of the specimen. The formula already mentioned was used to calculate the hardness number, and these numbers

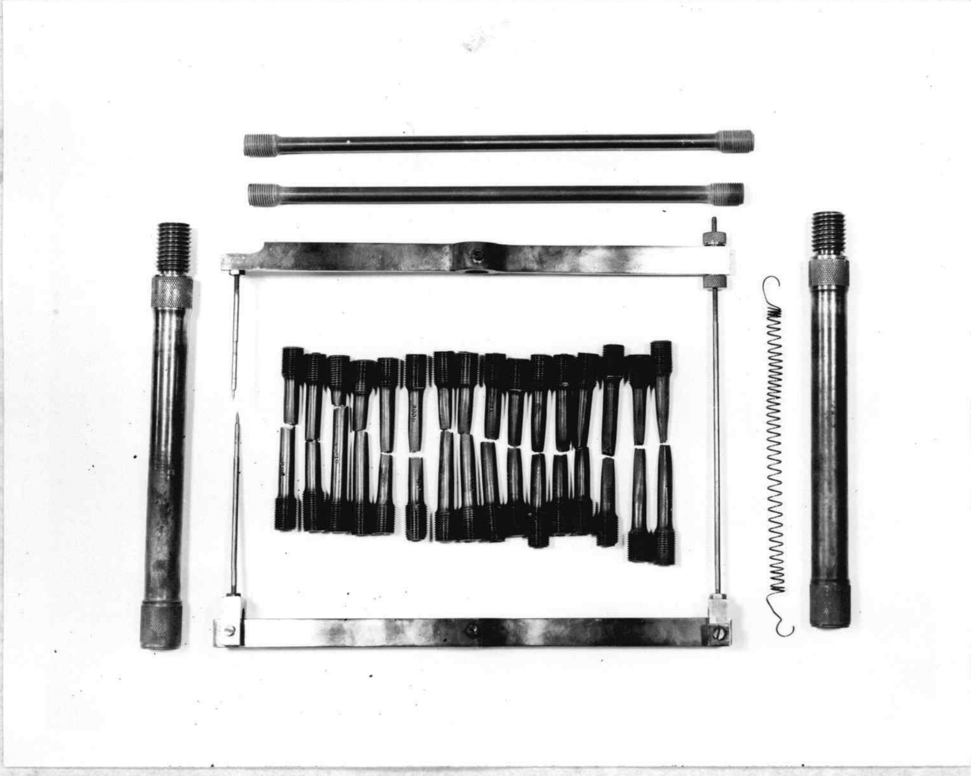

Figure 5. Specimens, Holders, and Extensometer.

Shows extensometer, specimen holders, tensile specimens, and modulus of elasticity specimens.

no. 2

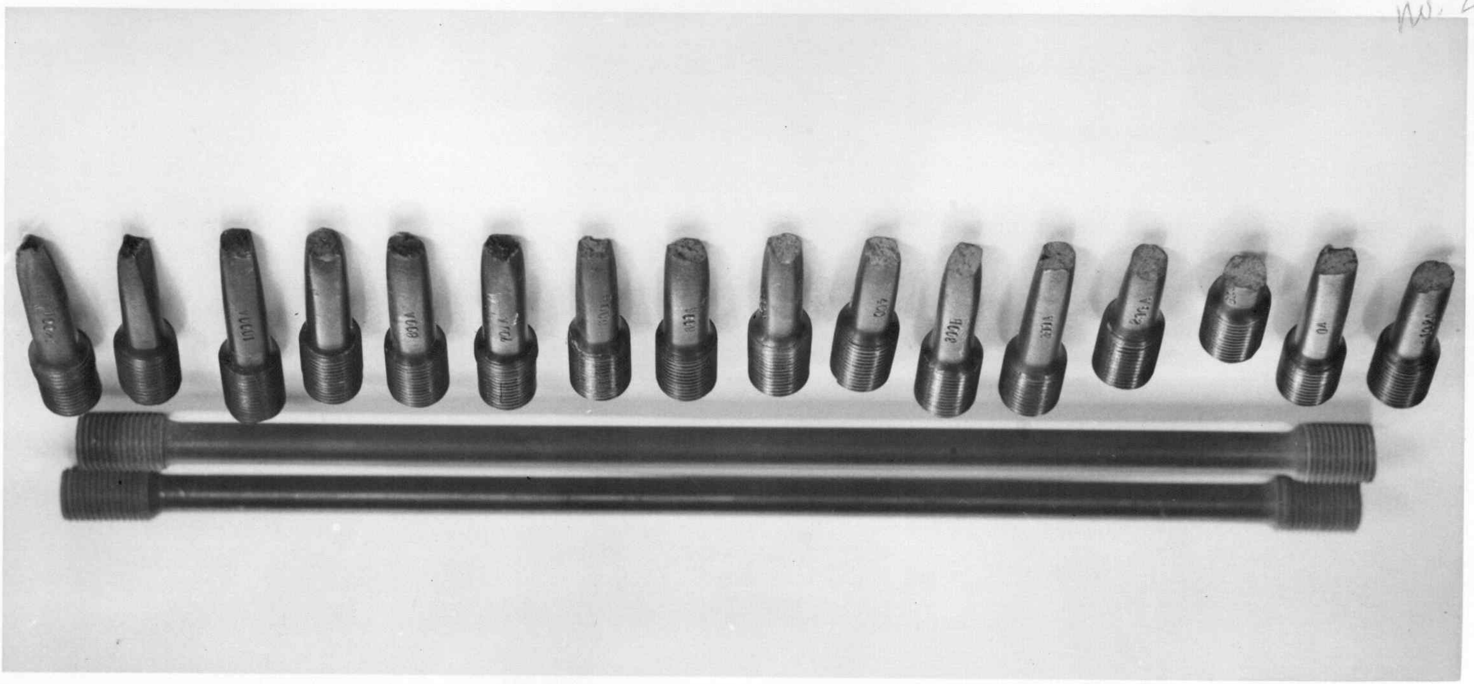

Figure 6. Specimens after Test.

Shows ends of broken tensile specimens and unbroken modulus of elasticity specimens.

were plotted immediately. Several check points were made to verify a doubtful point. The only bothersome difficulty involved in this test was the uncertainty of positioning the testing ball on the specimen. The problem was overcome, however, after a little practice.

RESULTS AND CONCLUSIONS

Since no important metallurgical changes occur in zirconium below 1570 F--the temperature at which the crystalline structure changes from hexagonal to body centered cubic--a discussion of these results will be limited to their accuracy and possible importance in regard to fabrication and design.

A list of the sources of error that will be discussed includes: Testing machine sensitivity, instrument calibration, thermocouple calibration, temperature fluctuation along the specimen, chemical uniformity of specimen, rate of loading, embrittlement due to oxygen absorption by the specimen at elevated temperatures, testing technique, and finally, accuracy and sensitivity of the extensometer. While the cumulative error from several of the above factors may lead to considerable inaccuracy in a particular point, and consequently render that point invalid or unreliable, it must be pointed out that the curve trends should be used as the criterion for accuracy. The author does not feel that any one experimental point, even though it lies on the curve, should be accepted as the true and accurate value for the property at that temperature. But he does feel that curve trends can be accepted with considerable confidence as a true picture of the variation of the particular mechanical property with temperature. And although some may not agree as to the exact path of these curves as they seek out the average of the test points, the consistency and regularity of the points defines quite definitely the general nature of the curve path. Since the highest test temperature was well below the temperature at which any significant crystalline structure changes occur, these curves would have their greatest value in the fields of fabrication and design. The peaks, depressions, and flat portions of the curves would seem then to be the information of most value, rather than some particular point, and they can be expected to give a reasonably accurate picture.

The Olsen testing machine used for this work, although not calibrated by the author just prior to use, receives frequent routine calibration tests and checks to within 1/4 to 1/2 per cent accuracy. At the loads used on the average specimen (ie 100 lb), the sensitivity of the calibration scale amounts to about 1 per cent of the total load.

Calibration of the Brown Electronik recorder and the thermocouples used has already been described under "Preparation for the Tests," and the results come within the reasonable limits of error set by the ASTM. ASTM specifications call for 0.25 per cent variation. The calibration data show that the accuracy of this instrument and thermocouples was within 1 per cent. The Leeds and Northrup potentiometer used for the low temperature work had been previously calibrated by a competent technician, and a calibration curve was used on all readings. The telescope used for reading the strain was first calibrated against a standard, and with the lenses used, one unit on the objective lens was equal to 0.1125 mm. With the aid of the movable hair line and vernier wheel, each of these divisions could be divided into approximately 1000 parts.

Any error introduced into the results due to fluctuation of the temperature during the testing or variation in temperature along the specimen could be accurately evaluated by inspection of the recording chart graph. For the ultimate tensile tests at high temperature chart inspection shows that very good agreement was obtained between the three thermocouples, and fluctuation in most cases was held to within 10 F or about 1 per cent. For the modulus of elasticity tests it was much more difficult to devise a test technique that would give small variation in

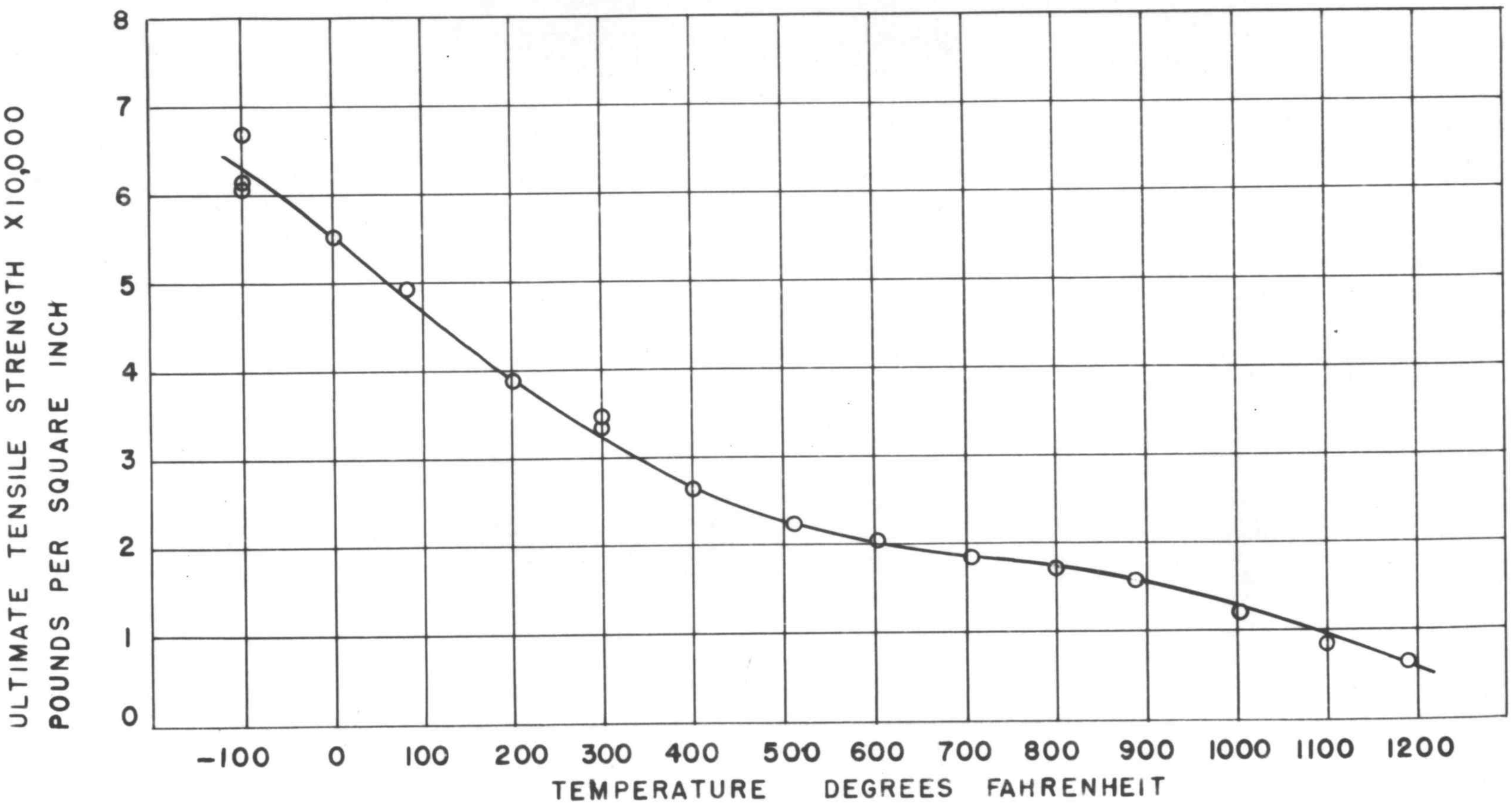

FIGURE 7 ULTIMATE TENSILE STRENGTH OF ANNEALED ZIRCONIUM

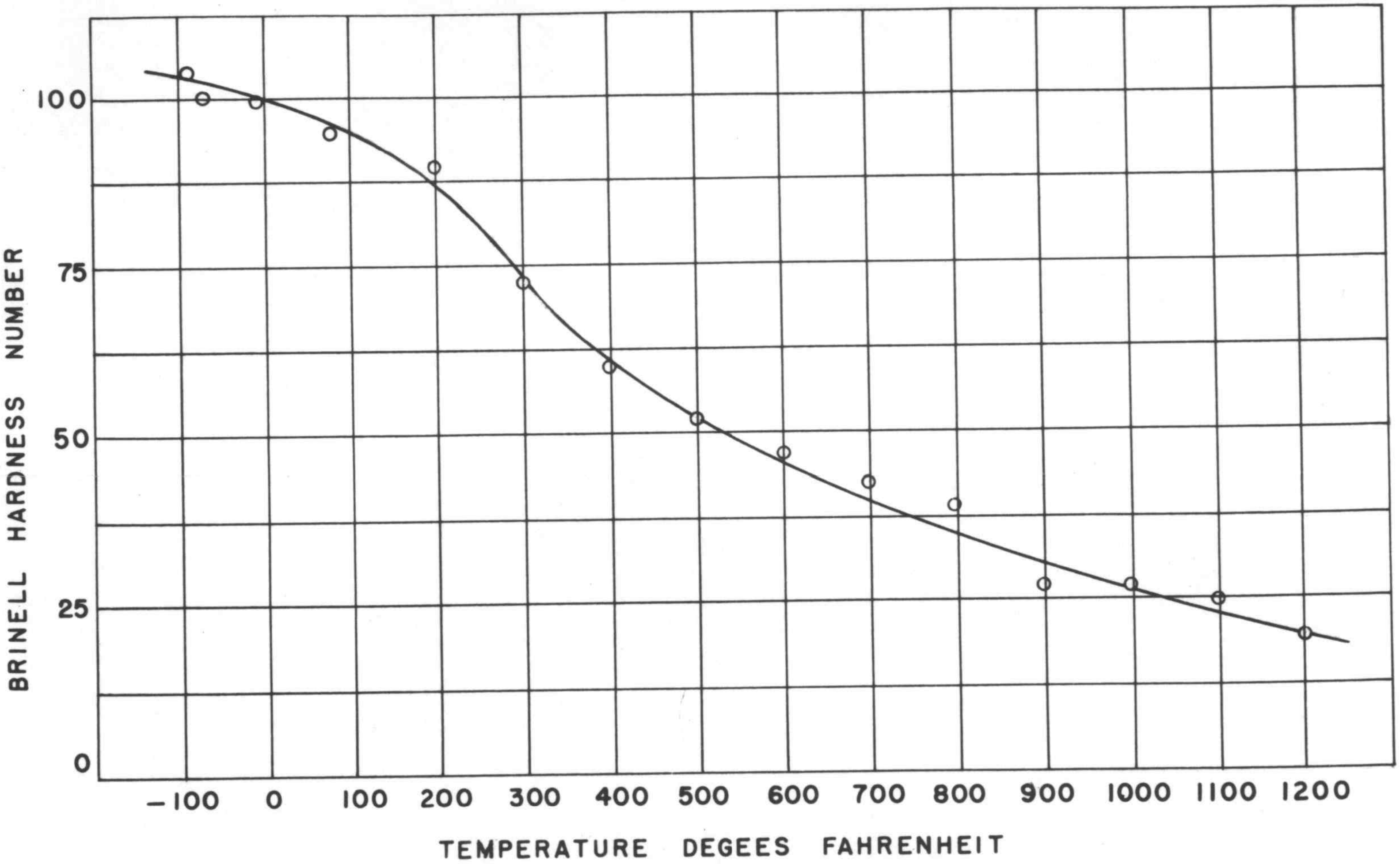

FIGURE 8 HARDNESS OF ANNEALED ZIRCONIUM

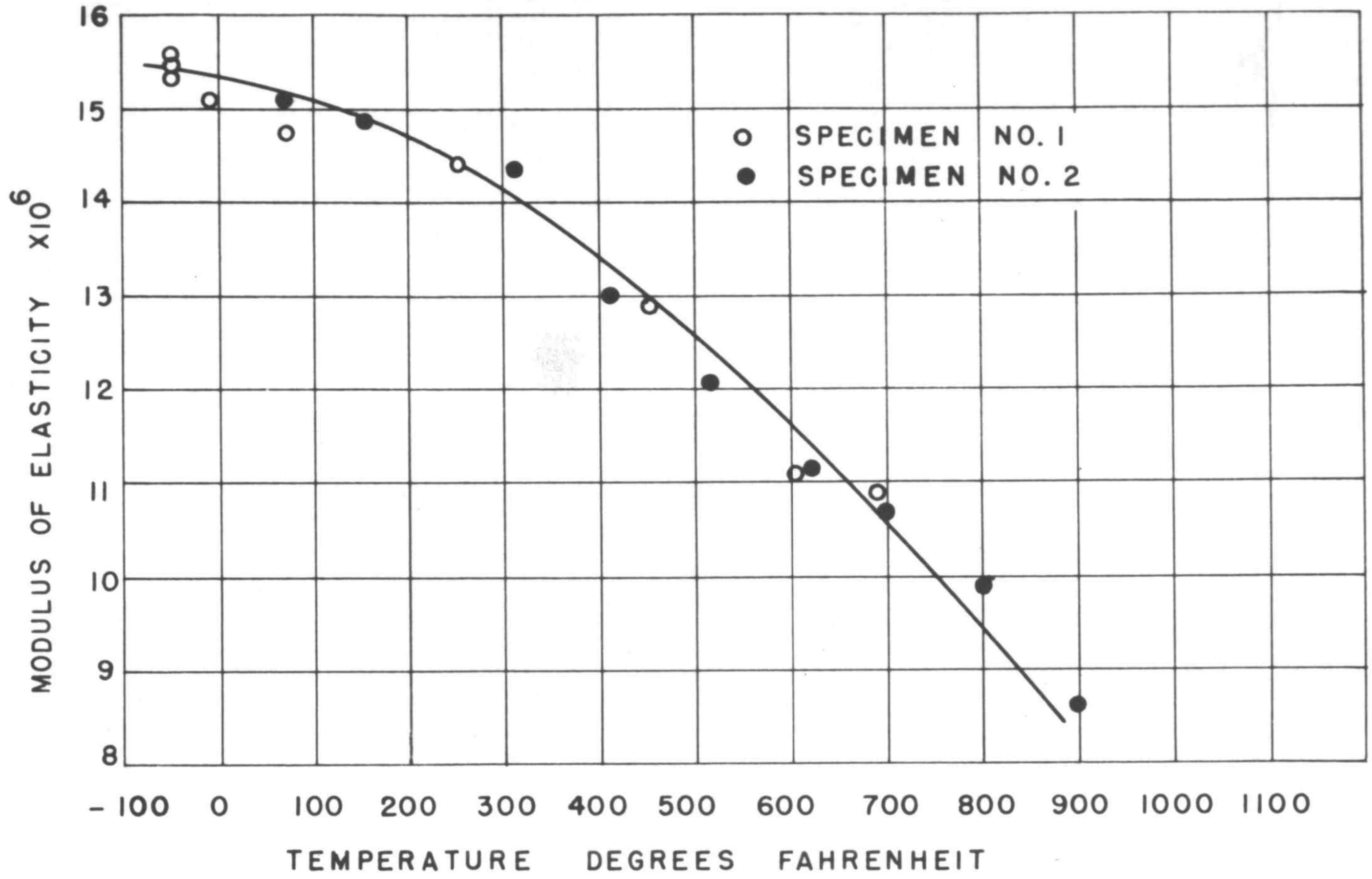

FIGURE 9 MODULUS OF ELASTICITY OF ANNEALED ZIRCONIUM

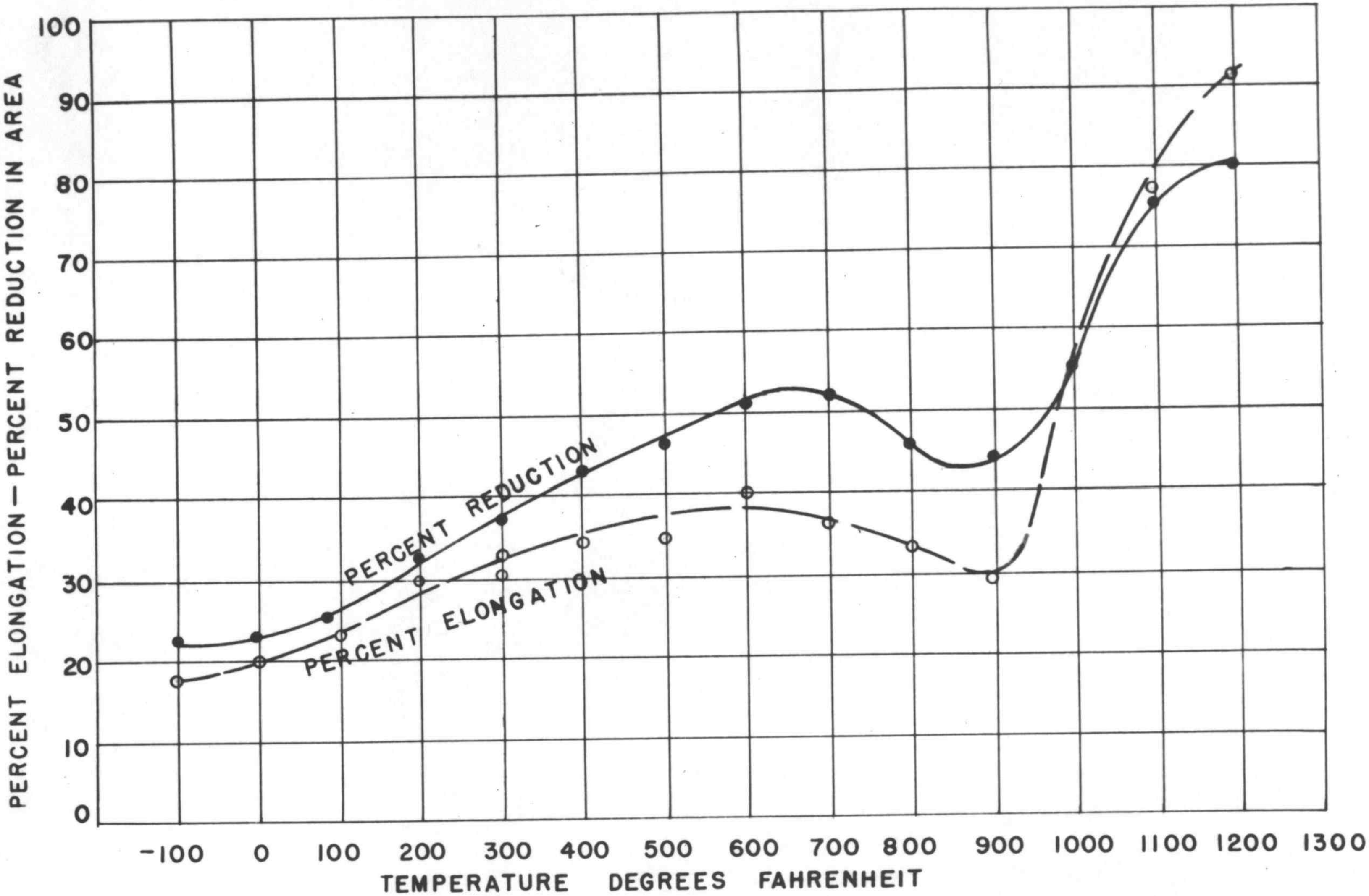

FIGURE 10 DUCTILITY CURVE OF ANNEALED ZIRCONIUM

temperature along the specimen, so that an average temperature had to be calculated from the three readings. This average might easily deviate from an actual value by 5 or 10 per cent, but was felt that the value of this point was not significant enough to throw the other test points out of line in establishing the curve trend.

The rate of loading as defined by ASTM is 0.05 inches per minute, and with the machine used a reasonably close value of 0.04 inches per minute was possible. The same rate of loading was used throughout the tests.

The possibility of oxygen embrittlement at the high temperatures was not a serious threat to the accuracy of the results, since in the mass form authorities do not consider this important below temperatures of 1200 F.

The only possible way of arriving at some figure to represent the accuracy of the extensometer used for the modulus tests is to analyze the overall picture and to make some conclusions by inspection of the variation of the individual test runs. Many of the points are off the curve drawn, but it can be seen that the trend of these points is well established and the value of the mechanical property is reasonable. The only dissatisfaction with the data may lie in the large variation of strain for each 100 lb applied. However, with the great number of readings taken, enough strain readings were obtained to be able to confidently pick out the readings that were close together and that did represent the largest percentage of all readings taken. Again it is the overall picture or curve trend that should in some measure verify the accuracy of the results.

The one factor that seems to overshadow all previous discussion of sources of error--having the greatest influence on the properties tested for--is chemical content. Discussion with those who have worked with various zirconium ingots and who have tested them reveals that startling variation exists in the purity of the metal even within a relatively small mass of metal. The actual degree to which the properties of the metal are affected is not known by this writer, but the effect of the impurities is believed possibly to be a larger source of error than any of those previously mentioned. This last discussion may in some way help to account for any difference existing between the values found from this work and the values reported from other sources on zirconium properties.

A summary of the amount and source of each error may be helpful here in evaluating the final results:

Testing Machine	
Accuracy	$\frac{1}{4}$-1%
Sensitivity	$\frac{1}{2}$-1%
Recorder and Thermocouples	1-2%
Potentiometer	0-$\frac{1}{4}$%
Telescope	0
Temperature Fluctuation	0-$\frac{1}{2}$%

Oxygen Embrittlement	0	
Loading Rate	0	
Extensometer	)	Unknown
Chemical Content	)	

Inspection of Figures 5 and 7, the ductility and hardness curves, indicates that a leveling off in the drop of ductility is accompanied by a leveling off in increased hardness at the lower temperatures; and that as temperature goes up, ductility is increased and hardness drops rapidly up to about 600 F. Between 600 F and 900 F, a sudden drop in ductility is observed which is followed by a drop in rate of hardness decrease. This is probably the temperature range that should be avoided in forming operations. Above 900 F the ductility jumps sharply upward, but it is not accompanied by any marked drop in hardness.

Looking at Figure 4, the ultimate strength curve, it can be seen that a leveling off in decreasing strength occurs in the 600-900 F range where the ductility drops off so rapidly. Beyond 900 F, the tensile strength then continues downward more sharply as the ductility increases on up to the 1200 F point.

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APPENDICES

APPENDIX A

These few notes on the cutting properties of annealed zirconium were taken in light of its recent greater abundance, and in the hope that they may be of some assistance to those planning to fabricate the metal.

The maximum feed on ½-inch stock was about 42 fpm with a 0.015 inch cut, without serious distortion of the work. The length of the work was 5½ inches dead center to chuck. The tool dulls quickly and must be kept sharp. Side rake should be about 5-10°, front clearance 5-12°, back rake 15-30°. Too great a front clearance dulls the tool quickly. The cutting oil was a water soluble fatty oil, and the cut left a smooth shiny surface on the metal. For threading operations, at 17 fpm cuts as deep as 0.005-0.007 could be taken without burring or distorting the work. The outside diameter expanded as much as 0.020 from taking deep cuts. In other words, starting with a nominal size of 0.490, after threading the diameter was 0.510. When the metal was hacksawed, it work-hardened very quickly and would dull a new blade after 1/8 inch penetration on ½-inch stock. Center drilling was the only drilling operation performed. Lard oil was used, and the chips came off readily and cleanly.

APPENDIX B

TABLE 1

DUCTILITY DATA, 1" GAGE LENGTH

Temperature, °F	Length	% Elongation	% Reduction Area
-100	1.18	18	23
0	1.20	20	23
81	1.20	20	25
200	1.30	30	32
300	1.32	32	37
400	1.34	34	43
500	1.34	34	46
600	1.40	40	51
700	1.36	36	52
800	1.33	33	46
900	1.29	29	44
1000	1.55	55	55
1100	1.77	77	76
1200	1.91	91	80

TABLE 2

HARDNESS DATA

Temperature, °F	Average Dia*	Brinell No.
-88	0.792 mm	100
-10	0.786 mm	99
80	0.808 mm	95.2
200	0.835 mm	89.5
300	0.920 mm	73.4
400	1.017 mm	60.1
500	1.100 mm	51.6
600	1.150 mm	46.8
700	1.190 mm	43.0
800	1.230 mm	40.8
900	1.480 mm	27.7
1000	1.480 mm	27.7
1100	1.580 mm	24.0
1200	1.700 mm	20.5

*Average of 3-4 indentations, 5-10 readings.

TABLE 3

MODULUS OF ELASTICITY DATA

Specimen No. 1		Specimen No. 2	
Temperature, ^{o}F	Δ*	Temperature, ^{o}F	Δ*
-47	0.251	70	0.248
-45	0.252	150	0.251
-43	0.256	310	0.260
-10	0.259	410	0.284
70	0.265	515	0.307
250	0.286	620	0.335
440	0.303	700	0.348
605	0.356	810	0.380
690	0.355	900	0.438
700	0.358		
800	0.397		

*Average total deformation representing 10-50 readings for 100 lb loads. 1 unit = 0.1125 mm.

TABLE 4

ULTIMATE TENSILE STRENGTH DATA

Temperature, ^{o}F	Tensile Strength, psi
-100A	60,300
-100B	67,000
-100C	61,300
0	55,000
81	49,000
200	39,200
300A	35,000
300B	33,400
400	26,400
510	22,500
600A	20,800
600B	21,000
705	18,800
800	17,500
890	16,000
1005	12,400
1100	8,800
1190	6,400