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Zirconium Metal–Water Oxidation Kinetics
I. Thermometry

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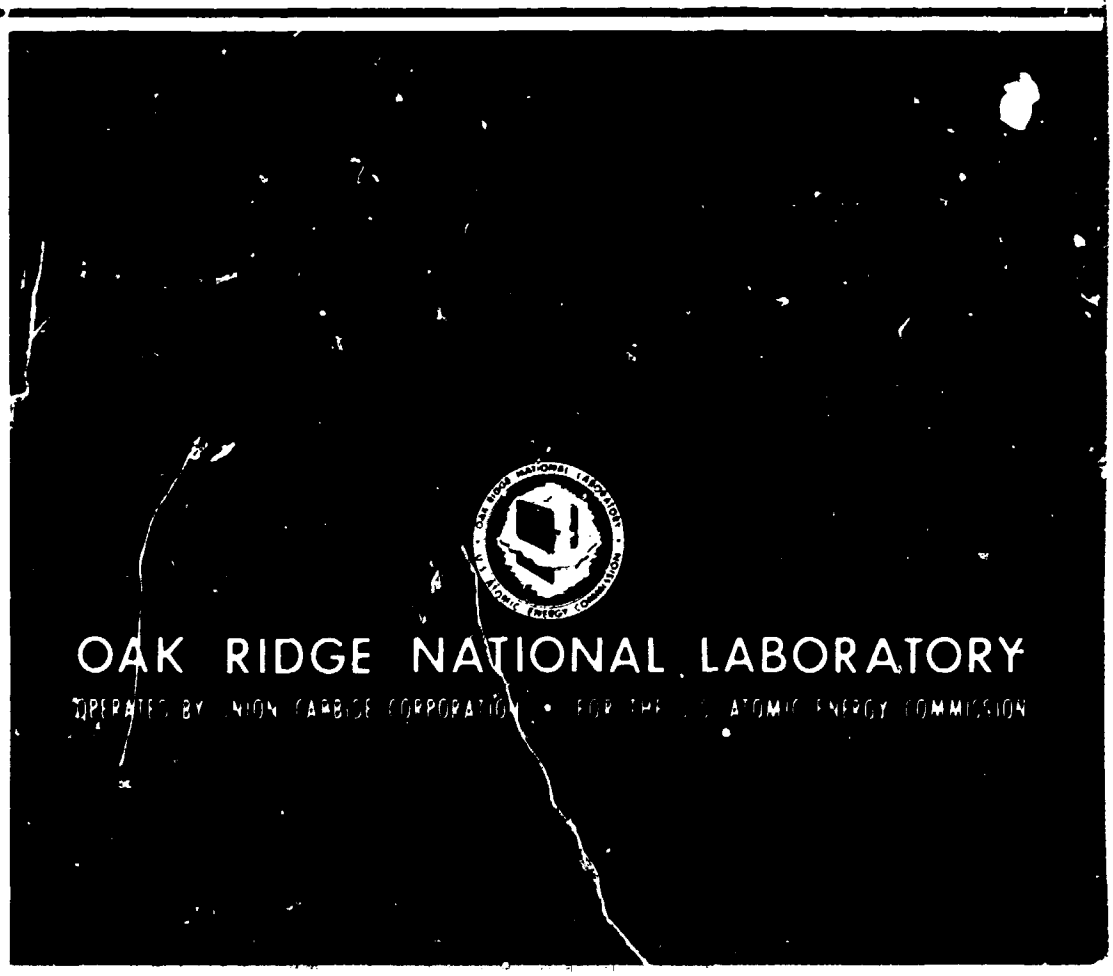

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METALS AND CERAMICS DIVISION

ZIRCONIUM METAL-WATER OXIDATION KINETICS
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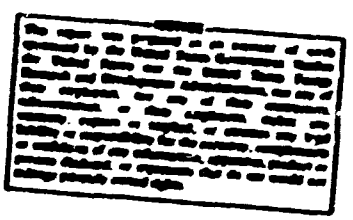
FEBRUARY 1976



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ABSTRACT

This report describes the thermometry techniques used in the Zirconium Metal-Water Oxidation Kinetics Program. Temperature measurements in the range 900 to 1500°C (1652–2732°F) are made in three experimental systems: two oxidation apparatuses and the annealing furnace used in a corollary study of the diffusion of oxygen in β-Zircaloy. Carefully calibrated Pt vs Pt–10% Rh thermocouples are employed in all three apparatuses, while a Pt–6% Rh vs Pt–30% Rh thermocouple and an optical pyrometer are used in addition in the annealing furnace. Features of the experimental systems pertaining to thermocouple installation, temperature control, emf measurements, etc. are described, and potential temperature-measurement error sources are discussed in detail.

The accuracy of our temperature measurements is analyzed in terms of the determinant and indeterminant errors of the system. We estimate the probable absolute accuracy of the temperature measurements in the oxidation apparatuses to be ±4°C (7.2°F) at 900°C (1652°F) and ±6°C (10.8°F) at 1500°C (2732°F). In the worst case we believe that we can specify temperature accurately to ±10°C (18°F). For the annealing furnace the probable temperature error approximates the determinant errors for the thermocouples, ±1°C (1.8°F) at 900°C (1652°F) and ±2°C (3.6°F) at 1500°C (2732°F).

INTRODUCTION

The goal of the Zirconium Metal–Water Oxidation Kinetics (ZMWOK) program is to characterize the oxidation of Zircaloy-4 in steam under conditions anticipated in a hypothetical loss-of-coolant accident (LOCA) in a light water reactor. The work consists of two experimental tasks: 1) the measurement of reaction rates of Zircaloy and steam under both isothermal and transient temperature conditions and 2) the determination of the diffusivity of oxygen in β-Zircaloy; both sets of measurements are being made over the temperature range 900 to 1500°C (1652–2732°F). In both tasks special efforts have been made to insure the accuracy of temperature measurements.

The importance of knowing the temperature at which a specimen is oxidizing can be illustrated by the following calculation. The temperature dependence of the oxidation rate constant, k, for Zircaloy is of the form

$$k = A \exp(-Q/RT) \qquad (1)$$

where A is a constant independent of temperature, Q is the activation energy, R, the gas constant, and T the temperature in degrees Kelvin. Figure 1 shows the percentage changes in k produced by errors in the measured temperature at various nominal test temperatures, assuming a value of 39,800 cal/mole for Q. As discussed below, the constraints imposed by the experimental necessity for measuring the temperature of a specimen immersed in flowing steam can easily lead to temperature errors well in excess of those shown in Fig. 1 and thus to unacceptably large departures from the true value of k at the nominal test temperatures. These results make it easy to suppose that at least a part of the scatter in oxidation data reported by previous workers is due to faulty temperature measurement techniques, and it is obvious that every effort should be made to minimize temperature errors, particularly systematic errors, in all future work.

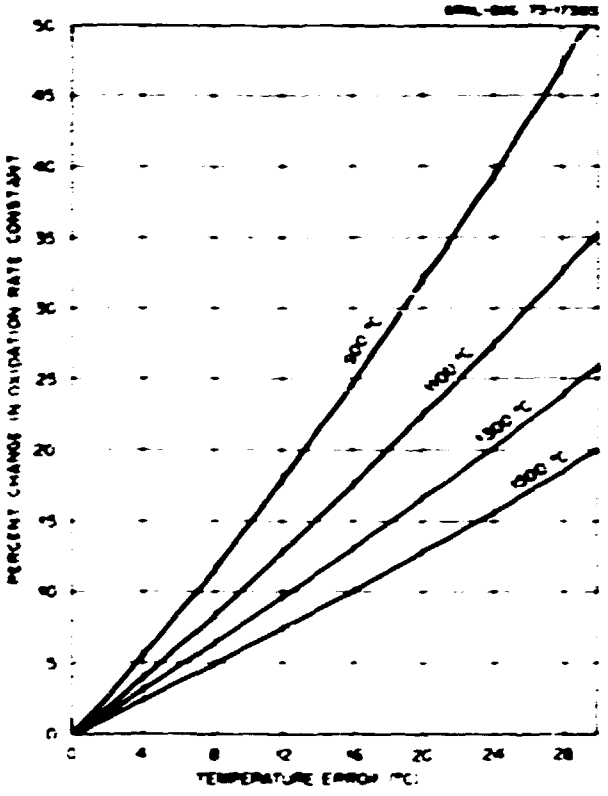

Fig. 1. Cross plot showing percentage change in oxidation rate constant as a function of temperature error at different temperatures.

A similar caveat is appropriate in diffusion studies in as much as a diffusion coefficient is also an exponential function of reciprocal temperature. The technical problems of temperature measurement during diffusion experiments are generally easier to cope with, however, in light of the fact that diffusion anneals are generally carried out in large, well insulated and shielded furnaces. Nonetheless, care must be exercised.

This report is a description of the temperature measurement problems encountered in the course of this program and of the steps taken to define and eliminate or minimize sources of temperature error.

TEMPERATURE MEASUREMENT TECHNIQUES

In both the oxidation and diffusion tasks nominal Pt vs Pt-10% Rh thermocouples (type S) are used as our primary means for determining temperature. In the diffusion experiments Pt-6% Rh vs Pt-30% Rh thermocouples (type B) are also attached to the specimens, and an optical pyrometer is used to obtain an additional check of the temperature.

Thermocouple Selection and Calibration

A prime goal in the Thermometry Task of this program was to provide temperature measurements traceable to the International Practical Temperature Scale of 1968 (IPTS-68). In the temperature range 630 to 1500°C (1652–2732°F), the IPTS-68 is based on two instruments: (1) the Pt vs Pt-10% Rh thermocouple, which spans the range 630.74 to 1064.43°C (~1167–1948°F), and (2) above 1064.43°C (~1948°F), a radiation pyrometer using the Planck Law of radiation with 1064.43°C (~1948°F), as the reference temperature and a value of 0.0143?? meter-kelvin for C_2 in the radiance equation.[2]

For this reason supplies of platinum and Pt-10% Rh reference grade thermocouple wire were obtained from the Sigmund Cohn Corporation.* Individual lots were fabricated from the same heat in order to minimize calibration differences. The Pt-6% Rh and Pt-30% Rh wires were ordered from Matthey Bishop, Inc.† Several wire diameters were specified, but subsequent testing revealed no differences in the performance of thermocouples made from 0.008, 0.025, and 0.051 cm (0.003, 0.010, 0.020 in.) diam wires. Therefore, for the sake of ease of handling, the 0.025 cm (0.010 in.) diam wire was used exclusively in all later experiments.

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*Sigmund Cohn Corp , 121 S. Columbus Ave. Mt. Vernon, N.Y. 10553.

†Matthey Bishop, Inc , Malvern, Pa. 19355.

Prior to calibration all thermocouple wires were subjected to an air anneal. The initial annealing schedule, 6 hr at 1300°C (2372°F), produced no difficulties with the pure platinum wire, but the tensile strength of the Pt–10% Rh was reduced by 30% and its total elongation by 45%. This deterioration of mechanical properties was shown metallographically to be related to excessive grain growth in the wire during the anneal; the average grain size after anneal was about half the wire diameter. Therefore, a less demanding annealing schedule was adopted: 2 min at 1400°C (2552°F), 20 min at 1200°C (2192°F), 1 hr at 1000°C (1832°F), and 2 hr at 500°C (932°F). This treatment produced wires composed of relatively small, equiaxed grains, and the mechanical properties of the wires were not degraded.

The actual calibration of the various thermocouple combinations was carried out in the Metrology Research and Development Laboratory, Instruments and Controls Division, Oak Ridge National Laboratory. The procedure used involved several comparison calibrations of the thermocouples wires to 1500°C (2732°F). Several thermocouples, including two NBS-calibrated Pt vs Pt–10% Rh thermocouples, were connected to a common hot junction and the emf values of various pairs compared with the standards. A detailed description of the calibration procedure is given in Appendix A.

The data obtained indicated that the thermoelectric properties of our wires were excellent. The Pt vs Pt–10% Rh wire behaved very much like the NBS-calibrated thermocouples, and calibration data for the Pt–6% Rh vs Pt–30% Rh thermocouples was also obtained. The temperature-emf relationships for the thermocouples are presented in the Appendix.

This calibration procedure represents an attempt to achieve, under ideal conditions, measurements of temperature with maximum uncertainty of ±2°C (3.6°F) on IPTS-68 at 1500°C (2732°F). Below 1064°C (1947°F), estimated uncertainties of thermocouple calibrations are less than ±0.2°C (0.36°F) at fixed points and less than ±0.3°C (0.54°F) for table values between fixed points.[3] These uncertainties increase above 1064°C (1947°F). At 1450°C (2646°F) an uncertainty of ±1°C (1.8°F) is given

for an NBS calibrated Pt vs Pt–10% Rh thermocouple, and we estimate an uncertainty of ±1.5°C (2.7°F) for our thermocouples at 1500°C (2732°F). Thus our goal of an uncertainty of ±2°C (3.6°F) at 1500°C (2732°F) appears realizable except for possible problems associated with thermocouple decalibration during installation and use.

We addressed this latter concern by submitting for recalibration a Pt vs Pt–10% Rh thermocouple that had been used in various experiments between 900 and 1475°C (1652–2687°F) for approximately 3 hr. This thermocouple was tested to 1000°C (1832°F), and the results of the recalibration (see Appendix) give no evidence of decalibration problems. Portions of a similar thermocouple were also submitted for chemical analysis (see Table 1). There was no indication of significant contamination which might lead to decalibration of the thermocouples.

A feature of our experimental procedure that mitigates decalibration difficulties is the fact that in a normal experiment the thermocouple hot junction is made by welding the thermocouple leads to a small tab of tantalum that is in turn welded directly to the specimen. At the end of an experiment the leads are clipped off just below the hot junction, and an entirely new hot junction is formed on the next specimen. Thus any contaminants near the hot junction are eliminated before they have time to diffuse far enough along the thermocouple wires to produce problems.

Thermocouple-Specimen Compatibility

The Zircaloy-steam reaction is highly exothermic ($\Delta H \approx 140$ k cal/mole in the temperature range of interest), and significant self-heating of a Zircaloy specimen can occur under conditions where the rate of oxidation is high. Therefore, in order to monitor accurately the temperature of an oxidizing sample, we considered it essential that metal-to-metal contact be maintained at all times between the specimen and the thermocouples.

Unfortunately platinum-base thermocouples cannot be attached directly to Zircaloy specimens used in experiments above ~1150°C (2102°F) because of the formation of a low melting [1185°C (2165°F)] Pt-Zr eutectic

Table 1. Spectroscopic Analysis of Pt vs Pt–10% Rh Thermocouples

Element	Analysis, ppm by wt, at positions[a]							
	1	2	3	4	5	6	7	8
Al	7	2	2	0.5	<0.1	0.1	0.1	0.3
B	0.4	0.4	0.3	0.3	1	0.3	0.4	0.3
Ca	0.5	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Co	50	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Cr	0.5	<0.2	1	0.5	0.5	0.5	0.5	0.5
Cl	7	7	10	5	7	3	7	5
Cu	300	7	20	0.7	7	0.7	7	0.7
Fe	50	20	20	5	20	5	50	3
K	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Mg	≤0.5	≤0.5	≤0.5	≤0.5	≤0.5	≤0.5	≤0.5	≤0.5
Mn	0.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Na	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Ni	7	3	3	0.2	3	0.2	5	0.2
P	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Pb	<1	<1	5	<1	<1	<1	<1	<1
Pd	1	<0.5	<0.5	<0.5	3	<0.5	<0.5	<0.5
Pt	M	M	M	M	M	M	M	M
Rh	M	M			M		M	
Sb	5	1	10	3	5	3	3	<1
Si	3	7	7	7	10	10	10	7
Ta	≤1	≤1	≤3	≤1	≤1	≤1	≤1	≤1
Ti	<2	<2	<2	<2	<2	<2	<2	<2
V	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Zn	5	<3	7	5	3	<0.5	<0.5	<0.5

[a] Position 1: Pt–10% Rh wire adjacent to hot junction.
Position 2: Pt–10% Rh wire at break between double and single bore insulation just below bottom of specimen.
Position 3: Same as position 1 except Pt wire analyzed.
Position 4: Same as position 2 except Pt wire analyzed.
Position 5: Pt–10% Rh wire at point where thermocouple exited furnace.
Position 6: Pt wire at point where thermocouple exited furnace.
Position 7: Pt–10% Rh control sample (annealed, as-received wire).
Position 8: Pt control sample (annealed, as-received wire).

(see Fig. 2.). We circumvented this problem by inserting tantalum or iridium tabs [2 x 2 x 0.075 mm (0.08 x 0.08 x 0.003 in.)] between the thermocouple and the specimen. The thermocouple leads were first spot welded to a tab with the ends of the leads separated by a distance of about 0.25 mm (0.01 in.), and the tabs were then spot welded to the specimen. The subsequent discovery of thermal gradients in the MiniZWOK oxidation apparatus (see below) led to a modification of the procedure in that the ends of the thermocouple leads were welded directly together on the tab so as to minimize the width of the hot junction.

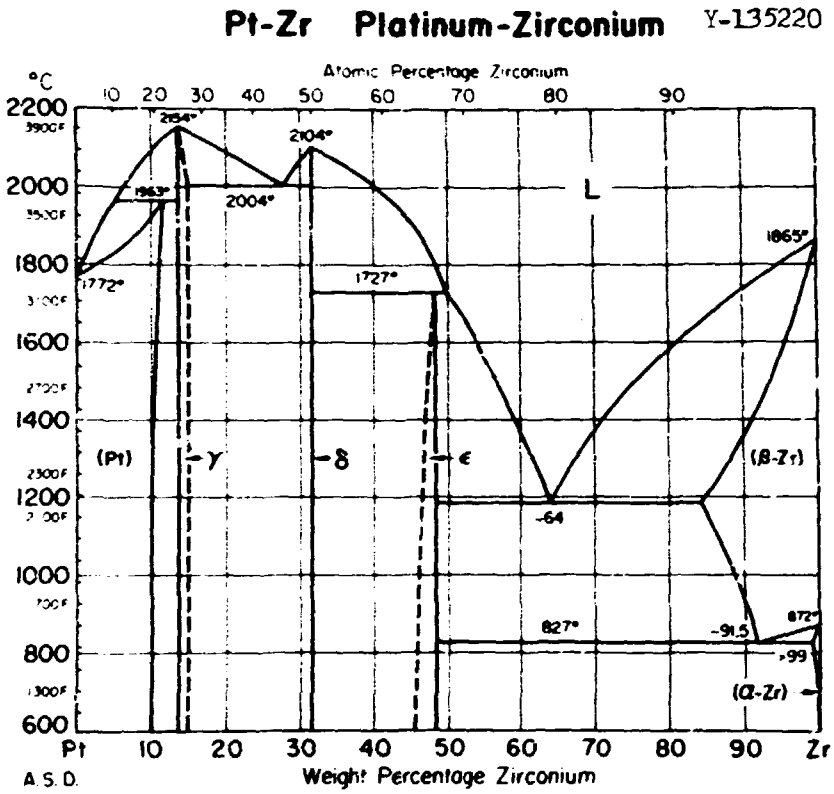

Fig. 2. Platinum-Zirconium phase diagram after Hawkins and Hultgren.[4]

Tantalum proved to be an excellent tab material when used in vacuum, as in our diffusion experiments, or in an inert gas, as in our low thermal inertia oxidation apparatus (see below). A Zr-Ta eutectic melting at ~1850°C (3362°F) has been reported[5] but produced no problems. A narrow diffusion zone between a tab and a Zircaloy diffusion specimen could be detected after a 30 min anneal at 1450°C (2642°C), Fig. 3, but because the junction between tab and specimen always consisted of metal with good thermal conductivity, we see no reason to question the validity of this form of thermocouple attachment. No Pt-Ta phase diagram appears to be available, but metallographic examinations of the Pt-Ta interface showed no sign of interaction. The only disadvantage of the tantalum tabs was the necessity to protect them from steam during our oxidation experiments.

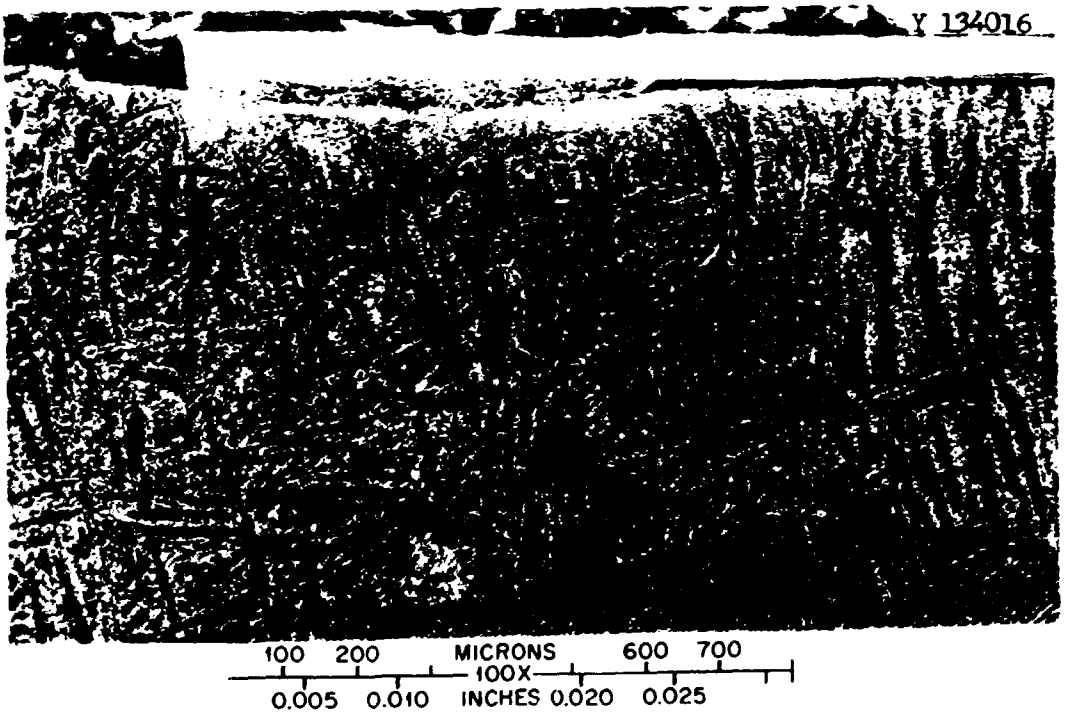

Fig. 3. Cross section through tantalum thermocouple tab spot welded to Zircaloy-4 diffusion specimen. Specimen was annealed in vacuum for 30 min at 1450°C (2642°F).

Because it is much more difficult to protect the thermocouple tabs in our second oxidation rate apparatus (see below), we employed iridium tabs for use in steam where, in the temperature range of interest, iridium is inert. We were unable to find a Zr-Ir phase diagram in the literature, and preliminary annealing tests[1] in vacuum did indicate the formation of a Zr-Ir eutectic between 1200 and 1300°C (2192–2372°F). However, in these tests the specimen was heated at a rate of 400°C/hr (720°F), thus providing ample time for interdiffusion between the sample and tab. In a much shorter test, in which a temperature of 1400°C (2552°F) was realized, carried out under the time-temperature regime shown in Fig. 4, the thermocouple did remain attached to the specimen throughout the experiment. Subsequent metallographic examination of the specimen (Fig. 5) showed evidence of liquation in both the tab and the specimen.

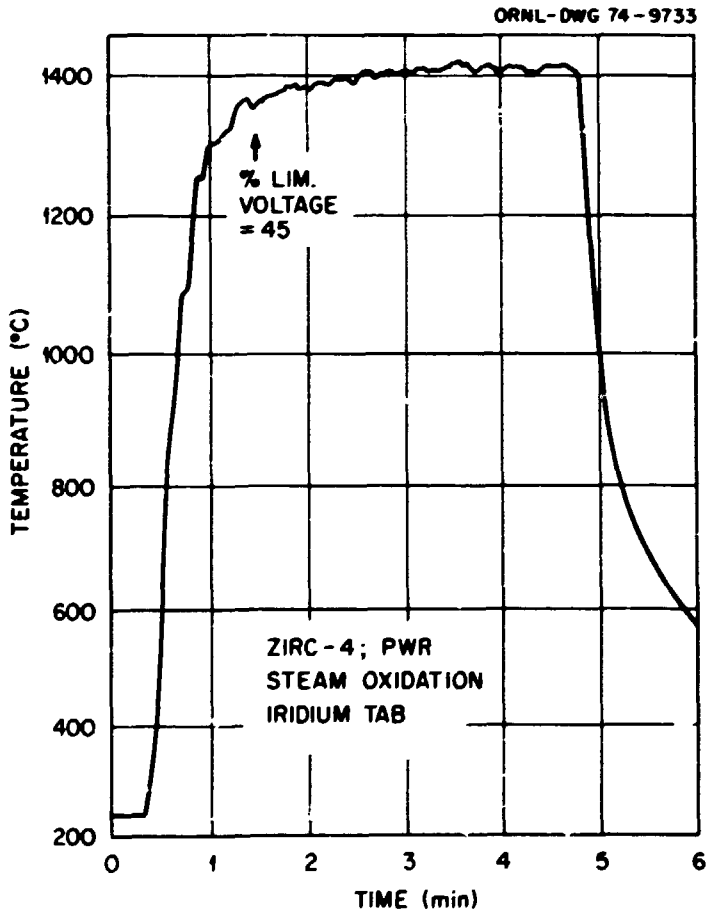

Fig. 4. Recorder trace of time-temperature regime used in test of iridium thermocouple tab on Zircaloy-4.

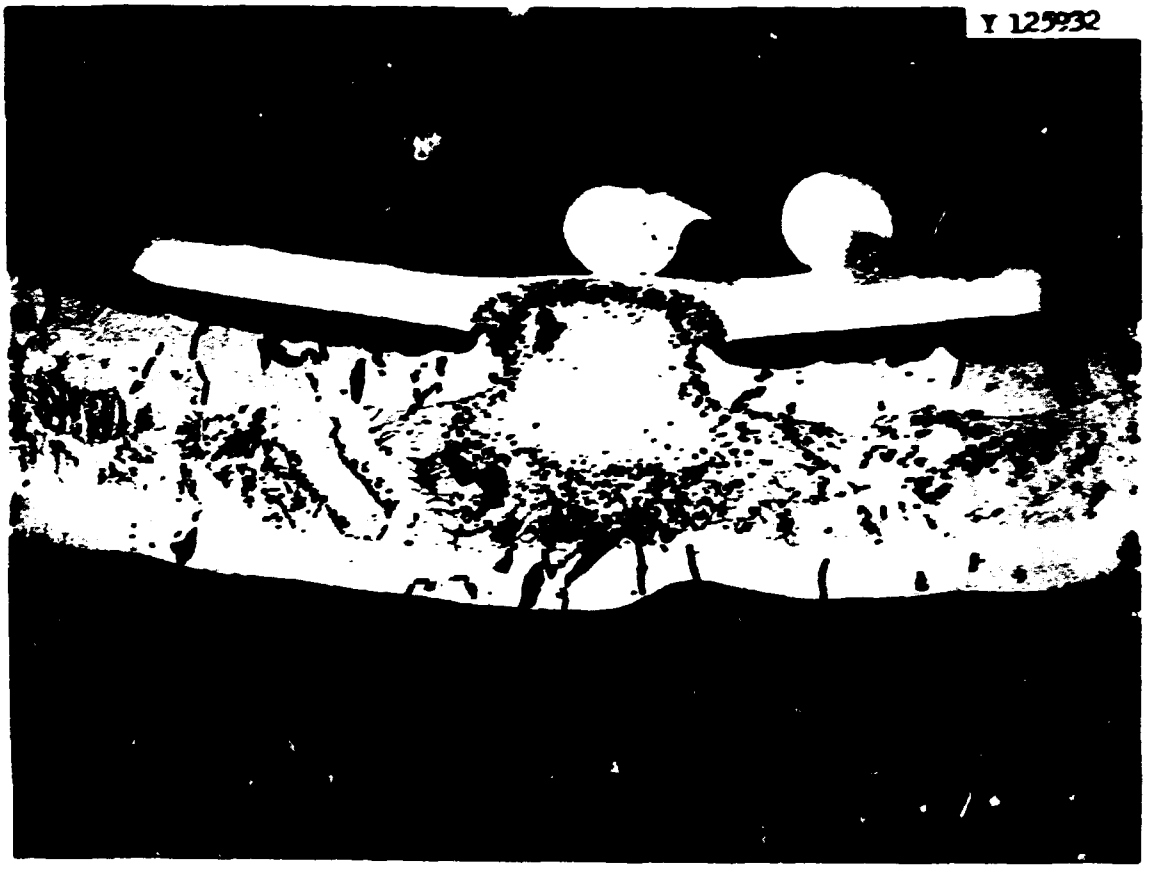

Fig. 5. Cross section of Zircaloy-4 PWR tube specimen after exposure in steam according to the temperature cycle of Fig. 4.1. Illustrates interaction zone associated with weld between iridium tab (on inside of tube) and specimen. As polished, bright field, 62x.

However, melting was confined to the immediate vicinity of the tab, the tab itself was not penetrated (thus protecting the thermocouple leads from attack), and good physical and thermal contact was maintained between the tab and specimen throughout the experiment. For these reasons and because we anticipate oxidation experiments of durations considerably less than 4 minutes at these very high temperatures, we are confident that iridium tabs can be used successfully as needed in our oxidation rate studies.

Optical Pyrometer

Two optical pyrometers were used in our diffusion studies. The first, available to us on an intermittent basis, was a Pyrometer Instrument Company photoelectric pyrometer which was calibrated relative to IPTS-68 using two NBS-certified gas-filled tungsten strip lamps. During the course of calibration and in subsequent periodic checks against an NBS vacuum tungsten strip lamp, small shifts [generally less than 1°C (1.8°F)] were noted in the pyrometer readings. These changes were attributed to a slight drift in the pyrometer reference lamp, and a systematic record of these shifts has been maintained so that these additional small corrections can be made in the pyrometer readings between major recalibrations. The total error[6] associated with the use of this instrument varies somewhat with temperature; at the gold point [1064°C (1947°F)] the error is ±1.7°C (3.1°F); at 1500°C (2732°F) it is ~±3°C (5.4°F).

The second pyrometer used was a Pyrometer Instrument Company Micro Optical pyrometer, manually balanced. This pyrometer was calibrated to 1300°C using an NBS vacuum tungsten strip lamp. The instrument readibility error resulting from this procedure was ±2°C (3.6°F), an error which is a part of the total instrument error (see Table 4, page 42).

CONTROL AND RECORDING OF TEMPERATURE

Three different apparatuses in which temperature measurements are required are being used in this program: an annealing furnace for the diffusion studies and two oxidation rate apparatuses that we have named "MiniZWOK" and "MaxiZWOK." In all three cases the design of the units was considerably influenced by the need to create experimental conditions under which temperature could be measured accurately, controlled properly, and recorded in an adequate manner. In this section we give description of the apparatuses and of the associated wiring, control, and recording systems.

Apparatus Description

MiniZWOK

The MiniZWOK apparatus is a low thermal inertia device used in the measurement of isothermal rates of oxidation and in controlled transient temperature experiments. It is shown schematically in Fig. 6. The reaction chamber consists of a 60 mm (2.36 in.) O.D. quartz tube 60 cm (23.6 in.) long with a Zircaloy-4 PWR tube specimen [30 mm long by 10.7 mm O.D. by 9.3 mm I.D. (1.18 x 0.42 x 0.37 in.)] supported at its center between two smaller quartz tubes. During an experiment steam flows past the outside surface of the specimen, and a slight positive pressure of helium is maintained inside the support tubes in order to prevent egress of steam to the interior of the specimen. A helium flow rate of ~0.2 cc/sec is used for this purpose.

The specimen is instrumented with three Pt vs Pt-10% Rh thermocouples. As described earlier, the hot junctions are formed by spot welding the thermocouple leads to small tantalum tabs [2 x 2 x 0.075 mm (0.08 x 0.08 x 0.003 in.)] that are in turn welded to the interior of the sample near its midpoint. One thermocouple is connected to the temperature controller, and the other two are used as measuring couples. In some experiments a separate tab was used for each thermocouple, but the more usual arrangement is to attach the control thermocouple and one measuring couple to a single tab and to position the second measuring couple on another tab mounted diametrally opposite the first.

This general design was adopted so that the thermocouple tabs could be protected from the steam and also to minimize thermal shunting effects. The latter purpose is also served by the tantalum heat shield inserted into the upper portion of the specimen. A lower heat shield is formed by the ends of the double-bore, DeGussit AL-23, high-purity alumina insulators used to separate the lower portions of the thermocouple leads. The upper parts of insulators are within the furnace and also serve to preheat the helium before it reaches the interior of the specimen.

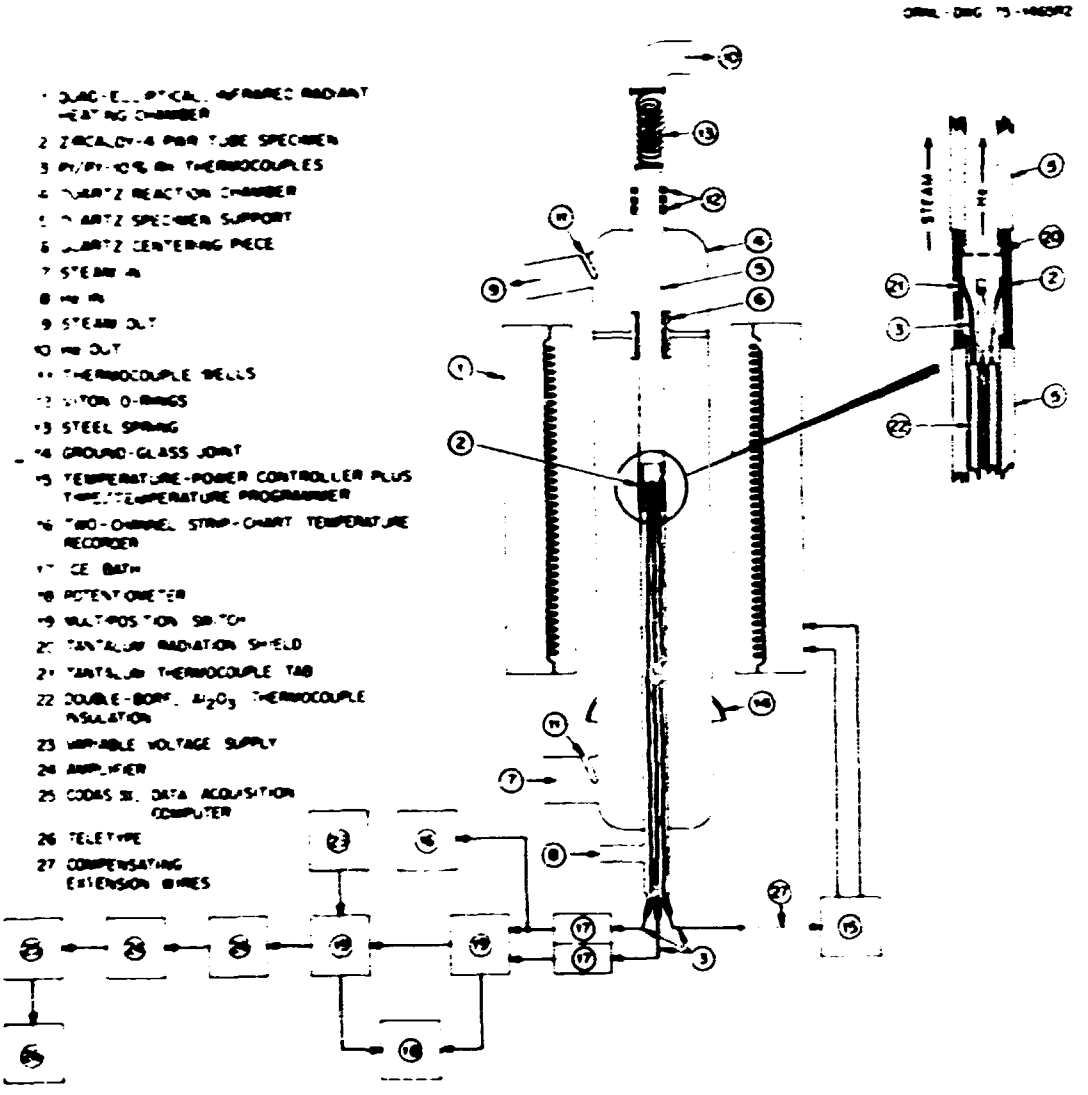

Fig. 6. Schematic diagram of the MiniZWOK oxidation apparatus.

The furnace surrounding the reaction chamber is a Research, Inc. quad-elliptical radiant heating chamber, Model E-4, with a hot zone of 25.4 cm (10 in.). Heating rates of 150°C/sec (270°F/sec) or higher can be attained with this unit, and the response of both the furnace and its controller is very fast. These characteristics plus the fact that the furnace is controlled directly by the specimen temperature prevent

specimen over-heating and allow isothermal conditions to be maintained during oxidation. A typical time-temperature recorder trace is shown in Fig. 7.

MaxiZWOK

This oxidation rate apparatus is shown schematically in Fig. 8. It differs from MiniZWOK in that the steam is preheated [max temp: ~1000°C (1832°F)] and the steam and furnace temperatures are controlled and fixed during an experiment. The specimen temperature is allowed to float, being determined by the combination of furnace and steam temperatures and steam flow rate. The latter is estimated to be ~80 km/hr (50 mi/hr) in most experiments. This corresponds to steam flow rates of ~1 lb/min.

The steam temperature is measured by a Pt vs Pt-10% Rh thermocouple suspended in the steam at the top of the ceramic reaction chamber. The reaction chamber is heated directly by a tubular resistance furnace whose temperature is measured by a stainless-steel sheathed Chromel-Alumel thermocouple inserted into the 0.3 cm (0.12 in.) wide annulus between the furnace wall and the reaction tube.

The specimen is a 46 cm (18 in.) length of Zircaloy tubing. A series of ventilation slots is cut into the lower portion of the specimen to allow free flow of steam through the interior of the tube and to reduce heat conduction from the upper end of the tube to its cooled lower end. The specimen is instrumented with three Pt vs Pt-10% Rh thermocouples welded to the outside of the tube, 120° apart at a point 5 cm (2 in.) from the upper end.

The instrumented specimen is mounted atop the plunger of a small hydraulic ram located in a distilled-water quench bath just below the reaction chamber. Once the desired furnace and steam temperatures and the appropriate steam flow rate have been attained, the specimen is driven up into the reaction chamber in 4 sec. At the end of the experiment the sample is again lowered in 4 sec into the quench bath. A typical time-temperature record is shown in Fig. 9.

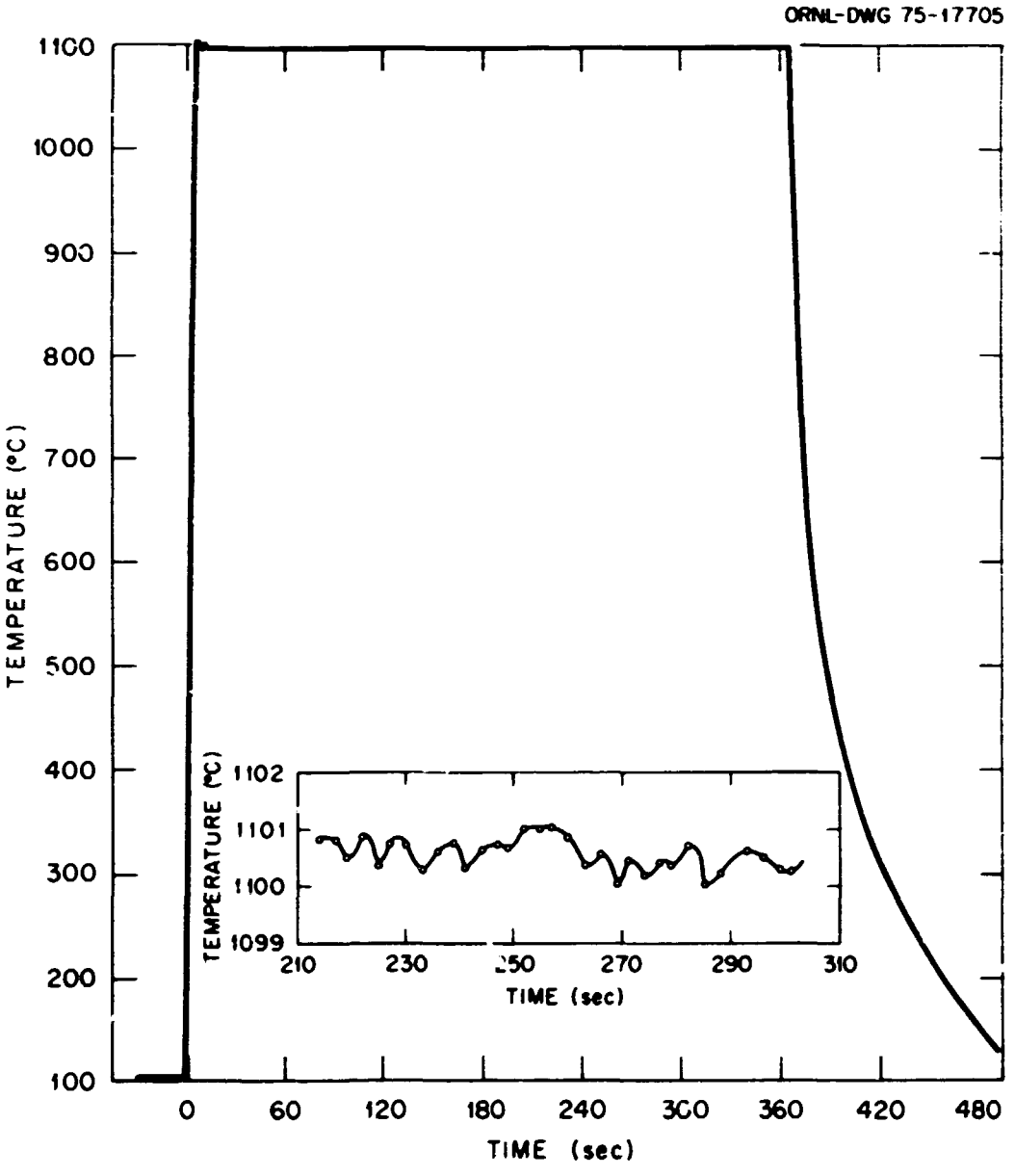

Fig. 7. Recorder trace of time-temperature record for a typical MiniZWOK experiment at 1100°C. Inset shows fine scale temperature fluctuations as recorded by CODAS.

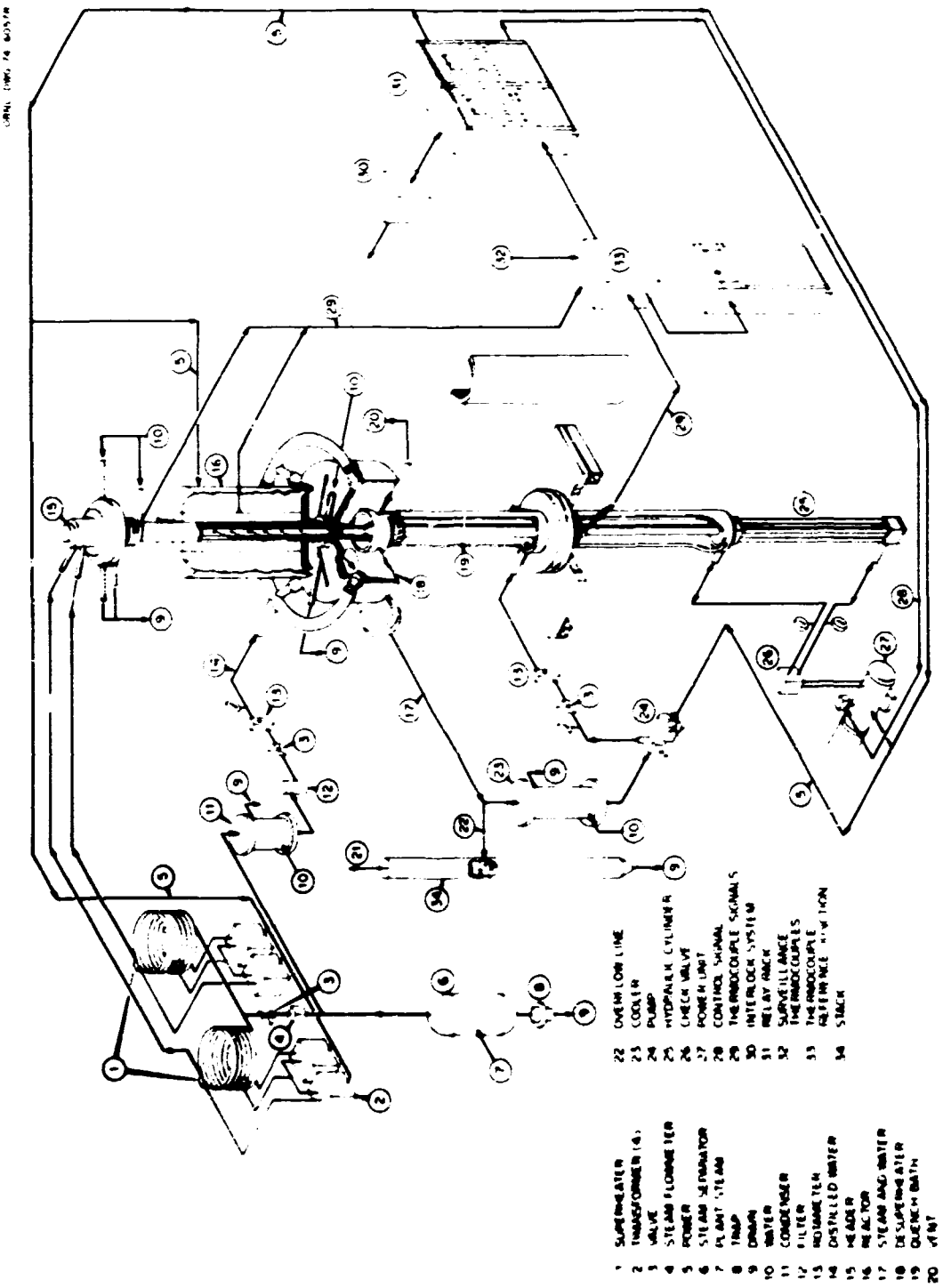

Fig. 8. Schematic diagram of the MaxiZWOK oxidation apparatus.

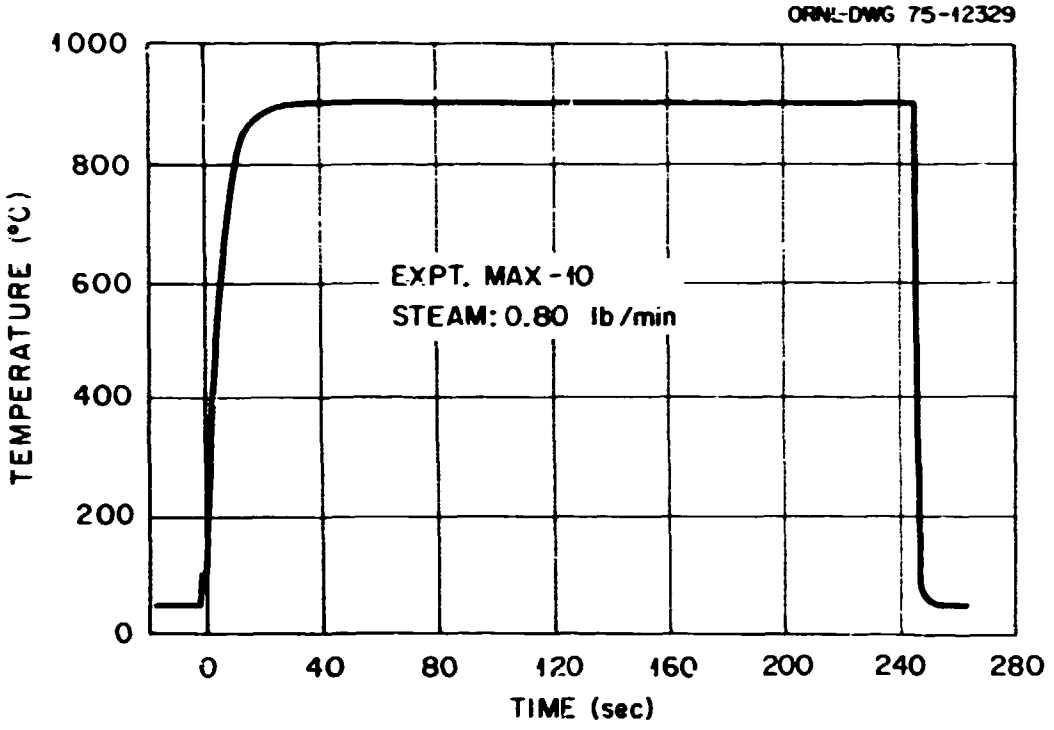

Fig. 9. Specimen temperature as a function of time for a MaxiZWOK oxidation experiment at 900°C (1652°F).

Diffusion Annealing Furnace

A tantalum split-shield furnace is used for the diffusion anneals (see Fig. 10). The specimens, which are Zircaloy disks, 11 mm (0.43 in.) in diam and 4 to 7 mm (.16–.28 in.) thick, are instrumented with two Pt–6% Rh vs Pt–30% Rh and one Pt vs Pt–10% Rh thermocouples welded to tantalum tabs attached along the circumference of the specimens. One of the Pt–6% Rh vs Pt–30% Rh thermocouples is used to control the furnace temperature, and the other two are measuring couples.

The specimen is located on a tantalum pedestal at the center of the tantalum split-shield heating element that is resistively heated. Multiple tantalum heat shields completely surround the furnace except at the top where an 8 mm (0.3 in.) diam hole provides optical access to a small crystal-bar zirconium cylinder [6 mm diam x 10 mm (.24 x .39 in.) high] positioned on the pedestal immediately adjacent to the diffusion specimen. A 1 mm (0.04 in.) diam hole drilled 8 mm (0.32 in.) deep into the top

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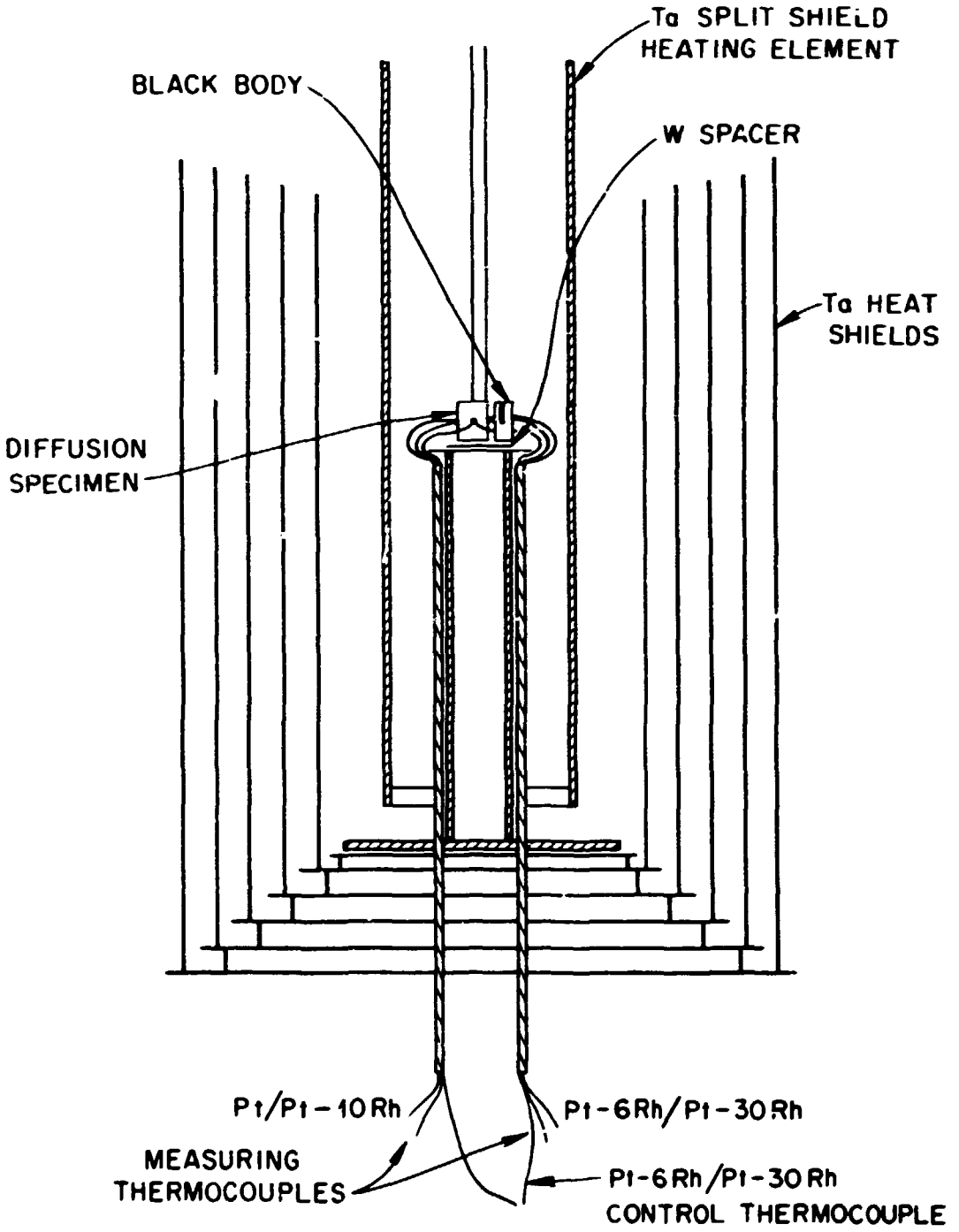

Fig. 10. Schematic drawing of annealing furnace used in diffusion experiments.

of the zirconium disk creates a black body used for temperature measurements with an optical pyrometer.

The entire unit is located inside a metal bell jar capable of being evacuated to pressures of 10^{-6} to 10^{-5} torr. A port at the top of the bell jar is fitted with an optically flat quartz window and a right-angle prism to provide an optical path for the pyrometer.

Wiring Procedures and Control and Recording Systems

In all three apparatuses the thermocouple wires are led-out of the system uninterrupted through ports sealed with silicone rubber or Teflon and from thence to an ice bath where they join low thermal emf copper telephone wires (see Appendix B).

Annealing Furnace

A schematic of the wiring and of the recording and control instruments is shown in Fig. 11. As may be seen, the copper wires from the control thermocouple go directly to an L&N Series 60 CAT controller. The other two thermocouples run to a "thermal free" switching station through which they may be connected to an L&N Speedomax-H recorder or a Honeywell Rubicon Model 2780 potentiometer. The output of the recorder is used only to follow the heating and cooling transients at the beginning and end of an anneal. Only long period temperature oscillations with amplitudes of $\sim\pm 1°C$ (1.8°F) are observed about the control point during an anneal, and for reasons discussed below in connection with the oxidation rate apparatuses, these oscillations have a negligible effect on the diffusion rate.

MiniZWOK

The instrumentation for this apparatus is the most complex of the three and is indicated schematically in Fig. 6. Temperature control is maintained with a Research, Inc. Model D-30 MicroThermac Controller associated with a Data-Trak Programmer, Model FGE-5110. The latter unit is programmable for virtually any time-temperature regime. The

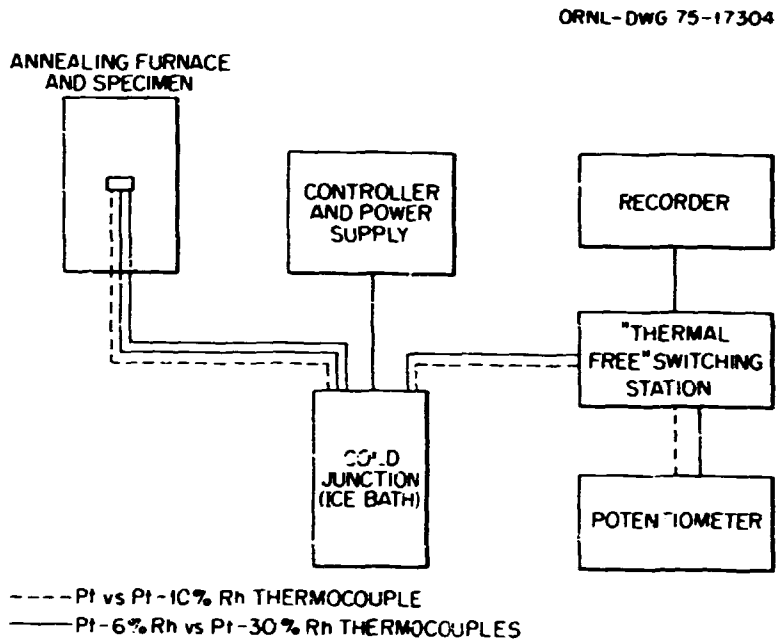

Fig. 11. Schematic diagram of instrument and wiring configuration for annealing furnace.

signals from the two measuring thermocouples after passing through a thermal free, multiposition switch (contact resistance < 0.001 ohm, thermal emf < 1 μV), may be 1) read on an L&N K-3 potentiometer, 2) recorded by a two-channel strip chart recorder (Esterline Angus, Model 1102S, a multi-span unit with calibrated zero), or 3) feed to computer operated data acquisition system (CODAS-III). The CODAS system has been described in detail elsewhere.[7] In our system the CODAS-III computer periodically reads the thermocouple emf (25 reading in 2 msec), calculates an average emf for the 25 readings, converts the emf to temperature according to the emf-temperature calibration for our particular Pt vs Pt–10% Rh thermocouple wires, and prints the time and the averaged temperature at ~2 sec intervals with the aid of a teletype. The CODAS-III system is calibrated directly before and after each experiment with a Dial-A-Source voltage unit (General Resistance, Inc., Model DAS-47A1) that itself is compared against our K-3 potentiometer.

Care was exercised in properly wiring, grounding, and shielding the various components of the MiniZWOK control and recording system in order to eliminate ground loops and other parasitic emf's. In addition it was found that considerable high frequency noise was introduced into the system by the operation of the silicon controlled rectifiers of the power supply for the quad-elliptical furnace. For this reason a low band pass filter with a cutoff above 50 Hz was installed between the multiposition switch and the CODAS amplifier (items 19 and 24 in Fig. 6). The filter, installed in each copper lead, consisted of a series-connected, 50 Ω, manganin-wire wound resistor grounded through a 60 μF mylar capacitor.

The temperature control of which this system is capable may be seen graphically in Fig. 7. Note the abrupt change from transient to isothermal control. In the isothermal control regions only small temperature fluctuations [~±1.0°C(±1.8°F)] about the control temperature occur.

MaxiZWOK

Power to the steam superheater is controlled by the signal from the Pt vs Pt–10% Rh thermocouple located at the upper end of the reaction tube (see Fig. 8). An ice bath cold junction is utilized, and control is provided by an L&N Speedomax H recorder-controller. The furnace temperature is controlled by the Chromel-Alumel thermocouple in the furnace annulus, again using a Speedomax H controller with a built-in temperature compensator. The measuring Pt vs Pt–10% Rh thermocouples are fed into two Esterline Angus, Model 1102S recorders; one of the couples is wired through an L&N DPDT, low-thermal-emf, copper switch so that its signal can also be read on the K-3 potentiometer. The calibration of the Esterline Angus recorders is checked before and after each experiment using a portable potentiometer; however, as in the case of MiniZWOK, the accepted temperatures are based on the K-3 potentiometer readings.

At the control temperature a MaxiZWOK specimen is subjected to temperature oscillations of about ±2°C (3.6°F). Two frequencies and amplitudes of oscillations were observed related to the independent control of the steam superheater and furnace temperatures.

Temperature Variations During Experiments

Virtually any temperature control system will produce temperature oscillations about a control point, and the magnitude of this effect in our three apparatuses has just been described. We also investigated[8] the effect of such oscillations on oxide and alpha layer growth in Zircaloy specimens in a series of computer simulated oxidation experiments. The types of temperature cycles investigated are illustrated in Fig. 12. Comparison of such results with those calculated for strictly isothermal oxidation showed that neither ξ-penetration values (the sum of oxide and alpha layer thicknesses) nor total oxygen consumption is sensitive to such temperature cycles. For example, over a 90-sec period for

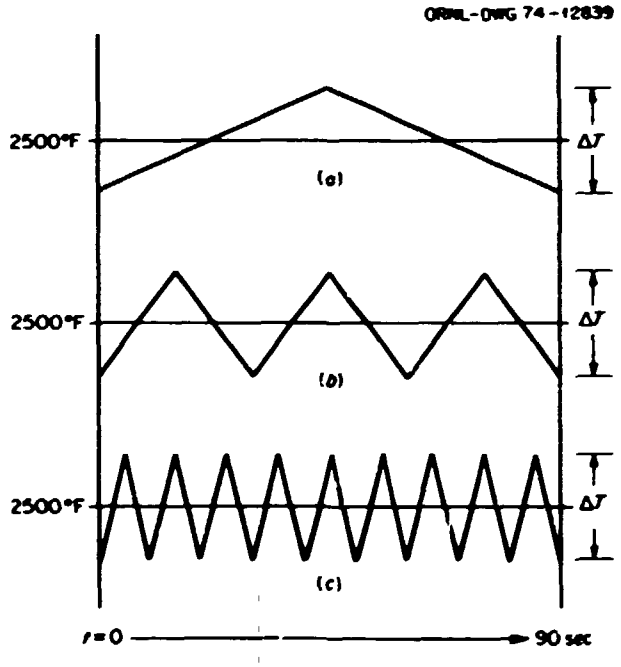

Fig 12. Cyclic temperature pattern used for computer simulated oxidation experiments; ΔT was varied up to 56°C (±28°C or ±50°F).

oscillations with a frequency of 10 sec^{-1} and an amplitude of ±28°C (50°F), differences of less than 0.5% in ξ and total oxygen were calculated.

Evidently, the average rate of oxidation is not changed appreciably by symmetrical temperature cycling about a mean. In light of the fact that oxygen diffusion in β-Zircaloy is the same kind of thermally activated process as oxidation, one may also conclude that our diffusion results are insensitive to this type of control problem.

POTENTIAL SOURCES OF THERMOCOUPLE ERRORS

Considerable care must be exercised in the use of thermocouples at high temperatures if serious temperature errors are to be avoided. This caution is particularly relevant in systems where experimental requirements create less than ideal conditions. We have considered the following list of potential error sources in relation to the Z2W0K program:

1. Thermal shunting
2. Electrical shunting
3. Parasitic emf's
4. Data acquisition system errors
5. Thermocouple calibration errors
6. Temperature gradients in the sample
7. Decalibration of thermocouples
8. Tab attachment effects.

In this section we discuss the error sources listed above as they apply to each of the three apparatuses used in the program.

Thermal Shunting

The term "thermal shunting" is used here to mean the shunting of heat to or from the thermocouple hot junction by convection, conduction, or radiation. The process is illustrated in Fig. 13 for the case of thermal shunting by convection. Cool steam flowing past the thermocouple

leads reduces their temperature and causes a flow of heat from the hot junction to the leads. As a result the hot-junction temperature is lowered with a consequent reduction in the emf generated by the thermocouple, and the indicated specimen temperature is erroneously low.

Thermal shunting errors, or "perturbation" errors as they are sometimes called, have been discussed by a number of investigators[9] who have made suggestions both for minimizing the errors and for calculating their magnitude.

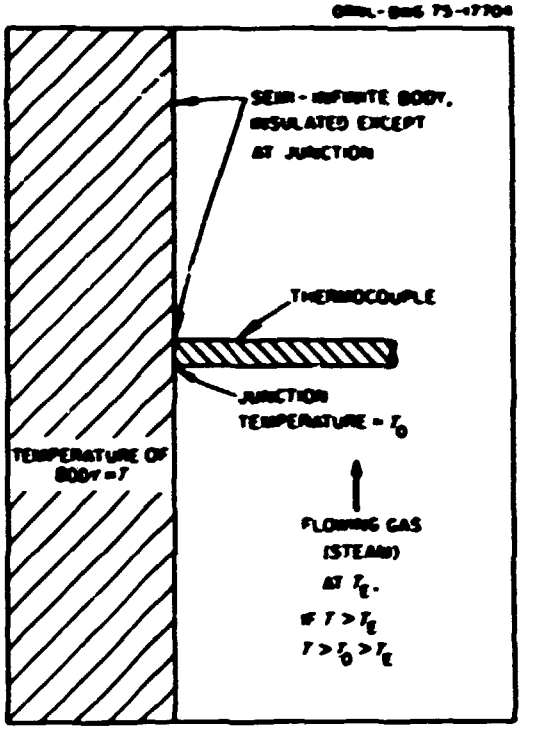

Fig. 13 Schematic model illustrating nature of thermal shunting errors.

The analytical problem is essentially one of establishing an acceptable model for the heat transfer system, and then solving the heat flow equations so that the temperature at a given point in the absence of the sensor can be calculated. While such solutions have been obtained[10-12] for several cases relevant to the operation of thermocouples on specimens suspended in flowing gas streams, these solutions are generally based on oversimplified system geometries. Obviously, under these

circumstances an experimental calibration of the system is desirable: but frequently it is impractical or even impossible, as in our case, to carry out such a direct calibration for a real system. For this reason we have taken the position that we should design our apparatuses in such a way as to minimize perturbation errors, while at the same time making use of existing computational procedures to estimate the magnitude of the errors involved and to guide the design work. Equations derived by Nusselt (reported by Jakob[10] and others) or Boelter[11] proved useful in the latter effort; and they have the added virtue that, because of the nature of the assumptions made in each derivation, the calculated perturbation error is believed to be greater than the actual error. Thus the results described below may be regarded as indicating the approximate maximum possible perturbation error in our experiments.

The equation reported by Jakob[10] is based on the following model: An infinitely extended, homogeneous body bounded by a plane surface is perfectly insulated against heat loss except for a small circular area. From this area, a cylinder or wire extends perpendicular to the plane surface into an environment having a temperature different from the uniform temperature of the body. The equation relates the temperature of the interface between the body and the wire to the temperatures of the body and its environment and to the several parameters that govern the flow of heat. The temperature perturbation created by a two-wire thermocouple is identical, at least for the ideal model, to that for a single wire. The heat flow from the junction into the wire is given by:

$$q_0 = \pi(2k_w h r_0^3)^{1/2}(t_0 - t_e) , \qquad (2)^*$$

where k_w = thermal conductivity of the thermocouple leads,
h = heat transfer coefficient between thermocouple leads and environment,
r_0 = radius of thermocouple leads
t_0 = temperature of the interface between body and environment (this is the temperature measured by the thermocouple),
t_e = environment (fluid) temperature.

*A typographical omission exists in Jakob's[10] presentation of this equation.

The flow of heat out of the body into the area created by the junction of the thermocouple lead is

$$q_c = 4r_c k(t - t_c) , \tag{3}$$

where r_c = the effective junction radius, assumed to be identical to the wire radius,

k = thermal conductivity of the body,

t = temperature of the body.

For steady-state conditions, the heat flows in Eqs. (2) and (3) are equal. Thus, combining the two expressions and rearranging:

$$t - t_c = \frac{\frac{\pi}{4}\sqrt{\frac{k_w h r_c}{g}}}{1 + \frac{\pi}{4}\sqrt{\frac{k_w h r_c}{g}}} (t - t_e) . \tag{4}$$

This expression affirms that the perturbation error $(t - t_c)$ in the temperature measurement depends upon the temperature difference between the body and its environment $(t - t_e)$, the thermal conductivities of the body and the thermocouple leads, and the heat transfer characteristics between the leads and the environment. Jakob also suggests an empirical expression for the heat transfer coefficient h which, when substituted into the above equation, results in a perturbation error that is independent of the thermocouple wire diameter. However, Otter[9] points out that in practice the wire size is generally a real variable.

Boelter et al.[11] analyzed the perturbation error for the temperature measurement of a thin plate with a cold fluid on one side and a hot fluid on the other. The thermocouple is mounted with its leads perpendicular to the surface of the plate in the hot fluid. Boelter's model is not directly applicable to the specimen geometry and heat-flow conditions in the MiniZWOK apparatus; however, within the limits set by the additional simplifying assumptions, the perturbation error should be similar for both cases. The analysis is based on a balance of heat transfer rates on the plate concentric about the thermocouple wire attachment area. The solution is given in several forms. Utilizing

several approximations that are valid for small perturbation errors, Boelter derived the following equation:

$$\frac{t - t_c}{t - t_e} = \frac{r_0\sqrt{2hk_w r_0}}{kb}\left[-\ln\left(\sqrt{\frac{\beta}{2}}\, r_0\right) - 0.577\right], \qquad (5)$$

where b = thickness of the plate, $\beta = (h_0 + h_i)/bk$, where h_0 and h_i are the appropriate heat-transfer coefficients on the opposite sides of the plate, and the other symbols have the same meaning as in Eqs. (2) and (3).

This equation shows the relationship between the perturbation error $(t - t_c)$ and the parameters of the system in a manner generally consistent with Eq. (4). The thermocouple and plate dimensions appear as more important variables in Eq. (5). This obtains, at least in part, because of the different geometries and because of Boelter's assumption that no temperature gradient exists in the plate normal to its surface. For minimum error, it is seen that the thermocouple leads should have a low thermal conductivity and a small diameter; the plate should be thick and of high thermal conductivity. In addition, if the effective heat transfer coefficient, h, between the thermocouple and the flowing fluid can be decreased by insulation or by positioning, then the perturbation error will be reduced accordingly.

Equation (4) was used to estimate the maximum perturbation error anticipated in our one-sided MiniZWOK apparatus. A major uncertainty in the calculation lies in the assignment of the fluid (helium or argon) temperature and flow characteristics in the vicinity of the thermocouple installations. Not only does this temperature enter directly into the equation for the perturbation error, but the heat-transfer parameters are also involved. For example, the effective heat transfer coefficient, h, between the fluid and the thermocouple wire can be calculated on the basis of forced convection at low flow rates or on the basis of natural convection with assumed temperature differences in the system.[13] Both

methods give the same value of h within a factor of 2 for low-conductivity gases such as air. If we assume that a reasonable value for the heat transfer coefficient between the inert gas in MiniZWOK and the thermocouple wires is 57 W m^{-2} $°K^{-1}$ (10 Btu hr^{-1} ft^{-2} $°F^{-1}$), about an order of magnitude higher than the steam-specimen heat transfer coefficient, then we can calculate an approximate value for the perturbation error. The thermal conductivity of the thermocouple wire, k_w, is approximately 29 W m^{-1} $°K^{-1}$ [40 Btu hr^{-1} ft^{-2} $(°F/ft)^{-1}$]; the thermal conductivity of the specimen, k, is taken as 31 W m^{-1} $°K^{-1}$ [18 Btu hr^{-1} ft^{-2} $(°F/ft)^{-1}$]. Therefore, substituting directly into Eq. (4), we obtain:

$$\gamma = (t - t_w)/(t - t_e) = 0.025. \qquad (6)$$

This result predicts that for bare-wire thermocouples extended at right angles into the inert gas stream the perturbation error will be 2.5% of the difference between the specimen and inert gas temperatures. The effective argon or helium gas temperature in the vicinity of the thermocouple installation is unknown. However, aside from circulation owing to convection, the flow rate on the inside of the tube should be very small, allowing the gas to be heated by contact with the components of the system that are heated directly by the radiant heating furnace. If, for example, the effective gas temperature in the cylindrical volume defined by the specimen is within 100°C (180°F) of the specimen temperature, then a maximum perturbation error of 2.5°C (4.5°F) would be anticipated. Of course, because our thermocouple installations are constructed to minimize this effect, the actual perturbation error should be less. As described elsewhere in this report, the experimental results are consistent with the prediction that the perturbation error is small for measurements of temperature in our one-sided MiniZWOK oxidation apparatus.

As emphasized earlier, the Boelter equation, Eq. (5), for plate specimens was derived with a different model and assumptions than those

employed for the case of the insulated semi-infinite slab. While we have no basis for ascertaining which of these treatments is best suited to describe our particular system, it is of interest to note that the Boelter expression leads to a similar value for the perturbation error when the same system parameters are used. For our case, the "plate" thickness is 0.686 mm (0.00225 ft); and we assume for purposes of calculation that the heat transfer coefficients on either side of the plate, h_o and H_i, are each 1 Btu hr^{-1} ft^{-2} $°F^{-1}$ (5.7 W m^{-2} $°K^{-1}$). The insertion of these values into Eq. (5) yields

$$\Sigma = (t - t_i)/(t - t_e) = 0.0336. \qquad (6)$$

Thus, Eq. (5) predicts that the perturbation error will be 3.36% of the difference between the specimen and coolant temperatures, which is quite close to the error predicted by Eq. (4). In addition, the error is only moderately dependent upon the particular values chosen for the plate heat transfer coefficient, Σ varying from about 4 to 2% as the coefficients change from 0.6 to 600 W m^{-2} $°K^{-1}$ (0.1–100 Btu hr^{-1} ft^{-2} $°F^{-1}$).

The results of these calculations are recognized as being approximate. Their contribution, therefore, lies not so much in a precise prediction of error values but in the fact that they indicate the relationship between some of the important system parameters that affect temperature measurement errors, thereby suggesting means for reducing these errors to a minimum. Our thermocouple installations are constructed with these ideas in mind.

Thermal Shunting in the MiniZWOK Apparatus

Our decision to construct the MiniZWOK apparatus as a one-sided oxidation system with steam on the outside and the thermocouples mounted internally was a direct consequence of the need to minimize thermal shunting effects. Errors on the order of 100°C (180°F) have been observed in systems where the thermocouples were exposed to rapidly flowing, cool steam.[14] A discussion of the magnitude of such errors may also be found

in Job.[10] In MiniWOK the thermocouples are subjected only to very slowly flowing helium, and the helium itself is preheated as it passes over the hot Al_2O_3 thermocouple insulation in the lower portion of the apparatus. In normal experiments the helium flow rate through the center tube of the apparatus is 0.24 cc/sec, and no changes in the measured emf's of the thermocouples were noted when helium flow rates were varied from 0 to 4.9 cc/sec (higher flow rates were not attempted) in the range of 900 to 1300°C (1652–2372°F), indicating the absence of any significant convective or conductive thermal shunting errors owing to the flow of helium past the thermocouples.

In order to minimize the possibility of radiative thermal shunting, a tantalum heat shield is located in the upper portion of the Zircaloy specimen (see Fig. 6). The Al_2O_3 thermocouple insulation located in the bottom specimen support tube also acts as a heat shield. However, radiation losses from the thermocouple leads appeared to be small in any case as we observed no change in measured specimen temperatures at a given furnace set point temperature with or without the tantalum heat shields.

As already noted the thermocouples used in this apparatus are spot welded to tantalum tabs, and the tabs, in turn, are carefully spot welded to the interior of the specimen tubes. The thermocouple wires are led away from the tab along the tube wall in a path parallel to the axis of the tube (supposedly the path with the minimum thermal gradient) to minimize conduction errors (see inset, Fig. 6). The vertical sections of thermocouple wire between the tabs and the double-bore Al_2O_3 insulation (see inset, Fig. 6) are covered with single-bore Al_2O_3 insulation. We have broken the single-bore insulation into small pieces to minimize heat conduction to or away from the hot junctions. However, comparison with unbroken insulation revealed no difference in the temperature measurement. Therefore, unbroken single-bore insulation is employed because it is easier to handle.

These various design features and tests have led us to the conclusion that thermal shunting errors in the MiniZWOK apparatus are negligible.

Thermal Shunting in the MaxiZWOK Apparatus

Thermal shunting problems in this apparatus are relatively minor because in isothermal experiments both the steam and the furnace are at the same temperature. Thus even though the thermocouples are exposed to rapidly flowing steam, there can be no cooling effect. The possibility of thermal shunting does arise in experiments in which substantial specimen self-heating occurs and in which the furnace temperature is higher than the steam temperatures. We expect such errors to be minimal, however, because 1) the difference between steam and specimen temperatures is relatively small - at most in the neighborhood of 200°C (360°F), and 2) since the furnace temperature in many cases is higher than the specimen temperature, the errors due to convective losses (steam effects) will be of opposite sign to those related to radiative effects (furnace wall temperature). In the worst case, using the perturbation error analysis above, we estimate errors due to thermal shunting to be no more than ~5°C (9°F).

Diffusion Annealing Apparatus

The constant temperature zone of the diffusion annealing furnace is relatively long [7.3 cm (3 in.)] and the anneals are carried out in vacuum (~1 x 10^{-5} torr). The furnace is also well shielded (see Fig. 10). Thus factors leading to thermal shunting are, in general, not encountered in this system. Their absence is borne out by the fact that for an anneal at a nominal temperature of 1150°C (2102°F) readings of 1149.4, 1149.6, and 1150.1°C (2100.9, 2101.3, and 2102.2°F) were obtained with a Pt-6% Rh vs Pt-30 Rh thermocouple, a Pt vs Pt-10% Rh thermocouple, and an automatic-balancing optical pyrometer, respectively.

Electrical Shunting

Thermocouple errors may arise due to electrical leakage of the thermocouple insulators or to thermionic emission between thermoelements

or other metals in the system. These errors can be as large as several hundred degrees Celsius in certain environments and at very high temperatures [e.g., in argon at a pressure of 43 torr and at temperatures near 1800°C (3272°F)].[6] However, in the current work this phenomenon was not a problem. For example, the resistance of an open circuit thermocouple at 1300°C (2372°F) in the MiniZWOK apparatus was 5×10^5 ohms and 1.7×10^5 ohms at 1455°C (2651°F), which are much too high values to allow significant electrical shunting. A similar experiment in the MaxiZWOK apparatus produced a value of $\sim 10^4$ ohms. The decrease in resistivity relative to that measured in MiniZWOK was attributed to the fact that the lower ends of the MaxiZWOK thermocouples are exposed to the distilled water of the quench bath for the apparatus; however, a resistance of 10^4 ohms was still considered sufficiently high to preclude the existence of significant electrical shunting. The best evidence for the absence of such effects in the diffusion furnace is the agreement between temperatures measured by the thermocouples and the optical pyrometer; even at 1500°C (2732°F) these differences were within the calibration error limits of the pyrometer.

Parasitic EMF's

Temperature measurement errors can be caused by the presence of parasitic emf's in the electrical circuitry of thermocouples. Reference here is made to such effects as ground loops, noise, pickup, and problems associated with the use of improper lead wires, reference junctions, feedthroughs, etc. The elimination of such error sources requires considerable care and the use of proper thermometry techniques. In setting up the circuitry for all our systems we worked closely with representatives of the Instruments and Controls Division of ORNL, and the steps taken to overcome these problems have already been outlined in the section on Control and Recording of Temperature.

Data Acquisition System Errors

Our primary standard used in measuring thermocouple emf's is a carefully calibrated Leeds and Northrup K-3 potentiometer or a Honeywell Rubicon, Model 2780, potentiometer. The accuracy of the former is given as 0.015% of the measured emf plus 0.5 μV, while that of the latter is 1 μV or 0.015% of the measured emf, whichever is greater. Thus at 1500°C (2732°F) for a Pt vs Pt-10% Rh thermocouple, each potentiometer has an accuracy of ~0.2°C (0.36°F).

For our MiniZWOK experiments time and temperature are also recorded with a Computer Operated Data Acquisition System (CODAS). This device is calibrated against the K-3 potentiometer at the beginning of each experiment, and recalibrations immediately after an experiment revealed no change. Thus for short periods of time the accuracy of CODAS appears to be comperable to that of the K-3 itself.

Thermocouple Calibration Errors

Thermocouple calibration procedures and uncertainty limits were described in detail in an earlier section. This uncertainty is greatest at temperatures above the gold point [1064°C (1947°F)], and we estimate it to be ±1.5°C (2.7°F) at 1500°C (2732°F). Below the gold point the uncertainty is ±0.8°C (1.4°F).

Temperature Gradients in the Sample

We have no evidence for the existence of temperature gradients within samples in the diffusion anneal furnace or in the critical part of the tubing used in the MaxiZWOK apparatus. The MiniZWOK samples, however, are not completely isothermal. There is a longitudinal gradient of ~4°C/cm (7°F/cm) from the center to the ends of the specimens. There is also a circumferential variation (two-fold symmetry) in temperature of ~7°C (13°F). The quad-elliptical furnace is built in two hinged sections that can be opened up to allow the insertion of the reaction tube.

The hinge and corresponding opening on the other side of the furnace are located along the vertical center line of two opposed elliptic hemi-cylindrical reflecting surfaces. The positions of the cooler regions on a specimen correspond to the positions of the hinge and opening, leading to the conclusion that these imperfections in the reflecting surfaces reduce the efficiency of the furnace in these areas.

These temperature gradients cause no particular problem for our measurements of oxide and alpha layer thicknesses since we simply section the specimen at the thermocouple tabs and make our metallographic measurements in the immediate vicinity of the tabs where the temperature is known. We did, however, investigate the possibility that, because of the Seebeck effect, the existence of such thermal gradients could lead to the generation in the thermocouple of an additional emf that is proportional to the temperature difference between the two wires of the thermocouple at the hot junction.

A calculation was performed for a thermocouple whose hot junction consists of successive segments of Pt, Ta, and Pt-10% Rh. A temperature gradient is assumed to exist across the junction with $T_1 > T_2 > T_3$, T_1, T_2 and T_3 being the temperatures at the Pt/Ta junction, the midpoint of the Ta segment, and the Ta/Pt-10% Rh junction, respectively. Let E_M and E_T be, respectively, the emf's generated by the thermocouple and a similar thermocouple in which the Ta segment is removed. It can be shown that

$$E_M - E_T \approx (S_{Ta} - S_{Pt})(T_2 - T_1) + (S_{Ta} - S_{Pt/Rh})(T_3 - T_2), \qquad (8)$$

where the S_x's are the appropriate absolute Seebeck coefficients. The results of this calculation are tabulated in Table 2 for the case $T_1 - T_3 = 1°C$ (1.8°F).

The "Worst Case Error" listed in the table was calculated on the assumption that the thermocouple leads are welded at the edges of the tabs, thus producing a hot junction length of ~2 mm. The worst temperature gradient in our sample is ~0.8°C/mm (1.4°F/mm), thus creating a temperature gradient of 1.6°C (2.9°F) across the hot junction.

In actual practice we attempt to keep the length of our thermocouple hot junctions at a minimum. Thus for a well made thermocouple junction the error due to the Seebeck effect should be at least an order of magnitude smaller than those listed for the "Worst Case."

The calculations given above were made for a Pt/Ta/Pt–10% Rh junction, whereas in actual practice the tantalum tab is attached to the Zircaloy tube. Thus the Zircaloy might also be expected to contribute to the Seebeck error. We have made a few rough determinations of the absolute Seebeck coefficient for Zircaloy-4, however, and find it to be approximately 1 μV greater than that for tantalum. Therefore, Eq. (8) may also be expected to give a reasonable estimate of the Seebeck effect temperature error for a Pt/Ta–Zr/Pt–10% Rh junction.

Table 2. Seebeck Effect Temperature Errors

Temp (°C)	$E_M - E_T$/°C (μV/°C)	$(E_M - E_T/dE/dT)$/°C (°C/°C)	(°F/°C)	Worst Case Error[a] (°C)	(°F)
900	−13.70	−1.2	−2.2	−1.9	−3.4
1100	−18.60	−1.4	−2.5	−2.2	−4.0
1300	−22.70	−1.9	−3.4	−3.0	−5.5
1500	−26.2	−2.2	−4.0	−3.5	−6.3

[a]See text.

Decalibration of Thermocouples

This problem was discussed in the section on Thermocouple Calibration Procedures. As indicated, we have found no indication of decalibration during times much longer than the duration of our experiments.

Tab Attachment Effects

As already pointed out, at temperatures above about 1100°C (2012°F) we find it necessary to insert small tantalum tabs between the Zircaloy and the thermocouples in order to circumvent the problem of the

low-melting Pt-Zr eutectic. The success of this arrangement obviously depends on establishing good thermal contact between the tabs and the specimen, and our normal procedure is to spot weld the tab to the specimen at several points. However, we have no way of determining prior to an experiment just how good the tab attachment might be, although in general it appears quite satisfactory. Note that "tab attachment effects" represent a special case of thermal shunting.

We have attempted to establish an upper bound for tab attachment errors in the MiniZWOK apparatus by performing an experiment in which one measuring thermocouple was attached to the specimen in the normal fashion while the second thermocouple was spot welded to a tab and the tab positioned in the approximate center of the specimen tube. Temperature differences of 9, 11, 10, and 15°C (16, 20, 18, and 27°F) were observed at 900, 1100, 1300, and 1500°C (1652, 2012, 2372, and 2732°F), respectively. In this experiment the flow rate of helium through the interior of the specimen was varied from 0 to ~5 cc/sec at each temperature; no change in the thermocouple readings was noted except at 900°C (1652°F) where a temperature drop of 1°C (1.8°F) was noted for the unattached thermocouple. These results set the maximum limits for temperature errors due to poor tab attachment.

Our regular experimental procedure requires an examination of both thermocouples and tabs after each experiment. Any indication of loose attachment, e.g., if the tab can be pulled loose with a pair of tweezers, causes us to regard that experiment as suspect. Any accidental leakage of steam into the interior of the specimen in quantities sufficient to produce significant oxidation of the thermocouple tabs also leads to the rejection of the experiment. Thus, in a normal experiment, errors due to poor tab attachment are expected to be much smaller than the maxima given above and should approach zero for good attachments.

One indication of the existence of tab attachment errors may be obtained by comparing the temperatures indicated by the two measuring thermocouples. Widely differing values suggest tab troubles. For example, if the tab to which the control and the first measuring thermocouple are attached makes poor thermal contact with the specimen,

the control thermocouple will sense a temperature lower than that of the specimen. The temperature of the specimen will thus increase until the emf required by the controller is generated by the control thermocouple. The first measuring thermocouple (attached to the same tab as the control thermocouple) will indicate approximately the expected temperature; however, the second measuring thermocouple (assumed to be well attached) will indicate a relatively high temperature – in this case the true temperature of the specimen.

The requirement that reasonable agreement exist between the two measuring thermocouple temperatures is not an absolute measure of tab attachment quality. Real temperature differences may exist in the specimen, spurious temperature differences may arise because of the Seebeck effect (see above), or the two tabs may both be poorly attached. With regard to the latter problem, the probability that the thermal attachment of both tabs will be equally poor seems small, but, clearly, the only real cure for tab attachment effects is to make sure that good bonding is achieved between tab and specimen, and we make every effort to see that that is done.

The above discussion applies primarily to the MiniZWOK apparatus. We consider tab attachment effects to be considerably less serious in MaxiZWOK and the annealing furnace because in these two apparatuses tabs, when used at all, are attached to the outside of the specimens, and problems of welding and weld inspection are substantially simplified.

EVALUATION OF TEMPERATURE ERRORS

In this section we consider the magnitudes of the total temperature measurement errors in our experimental systems.

Determinant Errors

Certain parts of the temperature measuring system used with a given apparatus may be calibrated against external standards, and a quantitative estimate of the error associated with each component can be obtained;

such errors are usually referred to as the determinant errors of the system. The determinant temperature errors for our three apparatuses are summarized in Tables 3 and 4.

Indeterminant Errors

It is considerably more difficult to specify quantitatively the indeterminant temperature measurement errors associated with our experimental systems. Indeterminant errors are those related to procedures or apparatus features not susceptible to direct, independent calibration as are, for example, thermocouples. Examples of such errors include the problems of thermal and electrical shunting, decalibration of thermocouples, tab attachment effects, and spurious emf's associated with temperature gradients across the thermocouple hot junctions (the Seebeck effect).

MiniZWOK

On the basis of evidence cited in the section on Error Sources we feel that errors related to thermal and electrical shunting and thermocouple decalibration are essentially negligible. Tab and Seebeck effect errors depend on the care exercised in installing the thermocouples. At worst they can amount to 15 to 20°C (27–36°F), but in general such gross errors are easily detected through post-test metallography and a direct examination of the tabs. In acceptable experiments, for reasons given in previous sections, such errors are expected to be much less than maximum, although we cannot give a quantitative estimate of their magnitudes.

MaxiZWOK

Again for reasons already given, we believe that electrical shunting and thermocouple decalibrations errors are negligible in this apparatus. Errors due to thermal shunting are also very small for isothermal experiments, although we estimate that such errors may reach 5°C (9°F) in our "mixed temperature" experiments where the furnace temperature

exceeds the steam temperature. The relative ease with which thermocouples may be installed and the absence of significant thermal gradients in this apparatus tend to minimize both the tab and Seebeck effects.

Annealing Furnace

The long isothermal zone of the furnace precludes the existence of Seebeck Effect errors in this apparatus, and tab installation procedures appear highly satisfactory (note the extensive bonding achieved between tab and specimen shown in Fig. 3, page 9). The other errors discussed above are likewise small.

Total Error Estimates

The total temperature error for a given apparatus is the sum of the determinant and indeterminant errors for the system. The determinant errors for the MiniZWOK and MaxiZWOK apparatuses are listed above and we have already cited evidence for our belief that the indeterminant errors are small. It is impossible to quantify them; however, in other studies[15] it has been observed that the probable absolute accuracy error of temperature measurements in a well designed system is two-to-three times the reproducibility. Thus, taking the determinant error as an estimate of reproducibility, we give as the probable temperature measurement error in MiniZWOK and for isothermal experiments in MaxiZWOK values ranging from ±4°C (7.2°F) at 900°C (1652°F) to ±6°C (10.8°F) at 1500°C (2732°F). In the worst case we believe that we can specify temperature accurately to ±10°C (18°F). During transient temperature tests in the MaxiZWOK apparatus where the temperatures of the steam, the furnace, and the specimen are all different, the temperature error will be slightly larger than that given above, the additional uncertainty reaching an estimated ±5°C (9°F) for those situations where, because of specimen self-heating, the specimen temperature is significantly above that of either the steam or the furnace.

Table 3. Determinant Temperature Errors in the MiniZWOK and MaxiZWOK Apparatuses

Error Source	Temperature Error, deg., at					
	900°C (°C)	1652°F (°F)	1200°C (°C)	2192°F (°F)	1500°C (°C)	2732°F (°F)
Uncertainty relative to IPTS-68	±0.3	±0.5	±0.7	±1.3	±1.0	±1.8
Thermocouple material variability	0.5	0.9	0.5	0.9	0.5	0.9
Potentiometer	0.16	0.28	0.19	0.34	0.24	0.43
Potentiometer read out	0.33	0.59	0.33	0.59	0.33	0.59
Thermal emf in copper leads	<0.01	<0.02	<0.01	<0.02	<0.01	<0.02
Reference (ice bath) temperature	0.01	0.02	0.01	0.02	0.01	0.02
Total	±1.3	±2.3	±1.7	±3.2	±2.1	±3.7

Table 4. Determinant Temperature Errors in Annealing Furnace

Error Source	Temperature Error, deg, at									
	900°C	1652°F	1344°C	1947°F	1200°C	2192°F	1500°C	2732°F	1900°C	2732°F
Thermocouples										
Uncertainty relative to NBS-ref										
Pt vs Pt-13% Rh	±0.3	±0.5			±0.7	±1.3			±1.0	±1.8
Pt-6% Rh vs Pt-30% Rh	0.5	0.9			1.0	1.8			1.5	2.7
Thermoelement material variability	0.5	0.9			0.5	0.9			0.5	0.9
Potentiometer error from										
Pt vs Pt-10% Rh	0.11	0.20			0.15	0.27			0.19	0.35
Pt-6% Rh vs Pt-30% Rh	0.13	0.21			0.16	0.28			0.19	0.34
Potentiometer reading error	0.10	0.18			0.10	0.18			0.10	0.18
Thermal emf in copper leads	<0.01	<0.02			<0.01	<0.02			<0.01	<0.02
Reference (ice bath) temp. error	0.01	0.02			0.01	0.02			0.01	0.02
Total thermocouple error for										
Pt vs Pt-10% Rh	±1.02	±1.80			±1.46	±2.62			±1.88	±3.38
Pt-6% Rh vs Pt-30% Rh	±1.2	±2.2			±1.7	±3.1			±2.2	±4.2
Automatic Balancing Optical Pyrometer										
NBS calibration error for strip lamp			1.5	2.7					2.1	3.7
Deviation of pyrometer table			0.05	0.09					0.11	0.21
"A" value error for window & prism			0.19	0.35					0.34	0.61
Error in determining reference lamp current			0.02	0.04					0.05	0.1
Total			±1.5	±2.7					±2.2	±3.9
Manually Balanced Pyrometer										
Error in calibrating strip lamp			1.5	2.7			1.5	2.7		
"A" value error for window & prism			0.19	0.35			0.34	0.61		
Instrument reproducibility error			2.0	3.6			2.0	3.6		
Total			±3.5	±6.3			±3.8	±6.9		

Additional evidence for the validity of our temperature error analysis is available from an examination of oxide layer thicknesses on the oxidized Zircaloy samples. Because of the thermal gradients in our samples or on account of small variations of the control point between experiments, we observe measurable differences in oxide thickness at different points around the circumference of a sample, differences that can be correlated with differences in temperature as indicated by our two measuring thermocouples. An extreme example of this effect occurred in an experiment where the nominal oxidation temperature was 1300°C (2372°F). One measuring couple read 1307°C (2385°F) and the other 1329°C (2424°F); the corresponding oxide thicknesses measured at the positions of the two couples were 53 and 57 μm, respectively. Because our preliminary results appear to agree well with the previous data of Hobson,[16] we can use the activation energy determined from Hobson's data to calculate oxide thicknesses expected at 1307 and 1329°C (2385–2424°F). The predicted values are 53 and 58 μm. While this result does not bear directly on the absolute accuracy of our temperature measurements, it does indicate that the random errors are small and well within the uncertainty limits given.

The only real way to quantify the indeterminant errors in experimental apparatus is to compare results obtained with those measured in a completely different apparatus or by a completely different method. We will be able to make such comparisons on completion of the data acquisition phase of the program, and expect to comment further in this regard in the final report on this project.

The total temperature error for the annealing furnace used in the diffusion experiments is somewhat easier to assess in that temperature measurements were made using both thermocouples and an optical pyrometer. Thus we have two independent checks on temperature. We compare these results in Fig. 14 where the reading of the Pt – Pt-10% Rh thermocouple is treated as the reference temperature, and the differences between that temperature and those indicated by the Pt-6% Rh vs Pt-30% Rh thermocouple and the pyrometer are plotted as a function of the reference temperature.

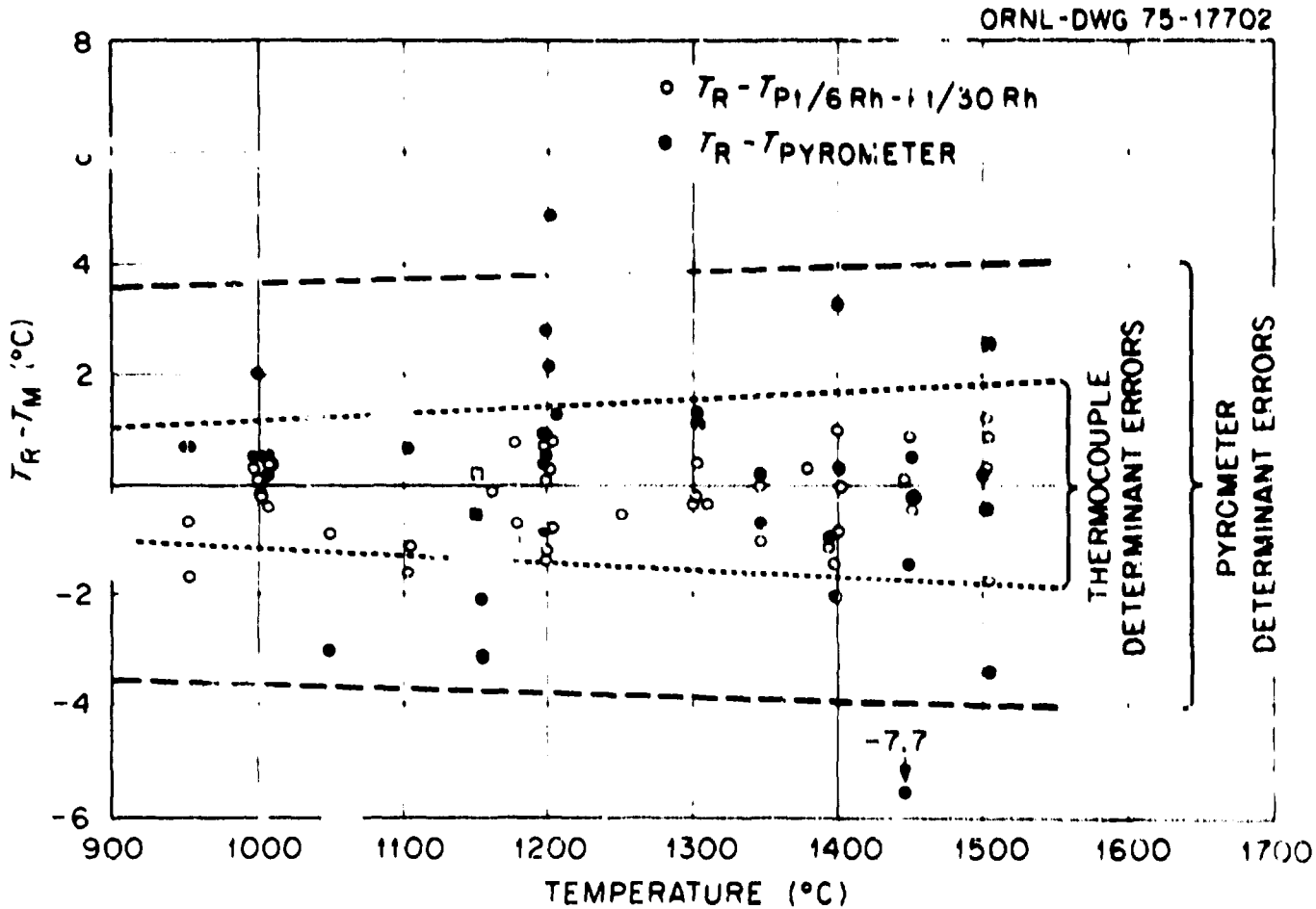

Fig. 14. Plot of temperature differences among thermocouples and pyrometer as a function of reference temperature. Temperatures, T_R, indicated by the Pt vs Pt–10% Rh thermocouple were taken as reference temperatures and compared with T_M, the temperatures of the Pt–6% Rh vs Pt–30% Rh thermocouple (open circles) and of the pyrometer (closed circles). The open and closed squares at 1150°C (2102°F) refer to measurements made with the Pt–6% Rh vs Pt–30% Rh thermocouple and the automatic balancing pyrometer, respectively.

As may be seen, more than 90% of the differences fall within the determinant error band for the thermocouples and only two pyrometer readings lie outside the corresponding error band for the pyrometer. We conclude, therefore, that the absolute error for our temperature measurements in the annealing furnace is not greater than the determinant error for the pyrometer [approx. ±3.7°C (6.7°F) at 1000°C (1832°F) and ±4°C (7.2°F) at 1500°C (2732°F)]. More likely, this error approximates the determinant error for the thermocouples [±1°C (1.8°F) at 900°C (1652°F) and ±2°C (3.6°F) at 1500°C (2732°F)].

Influence of Temperature Errors on Oxidation Rate Constant Determinations

As indicated in the Introduction, the oxidation rate constant is an exponential function of reciprocal temperature, and relatively small errors in temperature measurement can lead to large errors in the determination of the rate constant. The error relationships shown in Fig. 1 were calculated on the assumption that the rate constant was determined on the basis of one temperature measurement. In actuality our determinations of rate constants are based on ten different oxidation experiments of five different time durations, two experiments being carried out at each time. Thus, to the extent that our temperature measurement errors are random, our procedure tends to average out the effect of temperature errors.

In order to test the magnitude of this averaging we performed a series of computer simulation experiments in which the oxidation temperature was assumed to vary randomly in the interval $T - 10°C < \quad < T + 10°C$, where T is the nominal temperature of the experiment. The temperatures were distributed as a normal random variable with mean, T, with a 95% probability that they lay within the desired temperature interval. These temperature values were then fed into the standard oxidation rate equation

$$\xi^2 = kt \qquad (9)$$

where ξ is the total oxygen consumption in time, t, and $k = A \exp(-G/RT)$ where G, the activation energy, was taken as 39,500 cal/mole, and R and T are the gas constant and the true temperature respectively. The values of the t's selected were those actually used in our experiments. In order to normalize the k's, A was chosen as $\exp(G/RT_N)$, where T_N is the nominal temperature of the experiment; thus for the case where the temperature error is zero, the slope of a plot of ξ^2 versus t is unity.

On this basis a thousand oxidation rate curves were generated for each temperature considered and a least squares fit of their slopes obtained. The average and the standard deviation for each set of one thousand estimated slopes is summarized in Table 5.

Table 5. Average and Standard Deviation of 1000 Simulated Slopes
True value of the slope is $K(T) = 1$

Temperature (°C)	Average Slope	Slope Standard Deviation
900	1.00390	0.05668
1000	1.00048	0.05659
1100	1.00063	0.04583
1200	1.00014	0.03476
1300	1.00039	0.03123
1400	1.00025	0.02535
1500	1.00012	0.02221

A more meaningful display of these same data was obtained when the range of values of the estimated slopes was divided into intervals and the frequency of occurrence of the values in each interval plotted in histogram form. The histogram for the 1300°C (2372°F) is shown in Fig. 15. As might be expected for a normally distributed variable, it was found that at all temperatures at least 95% of the estimated

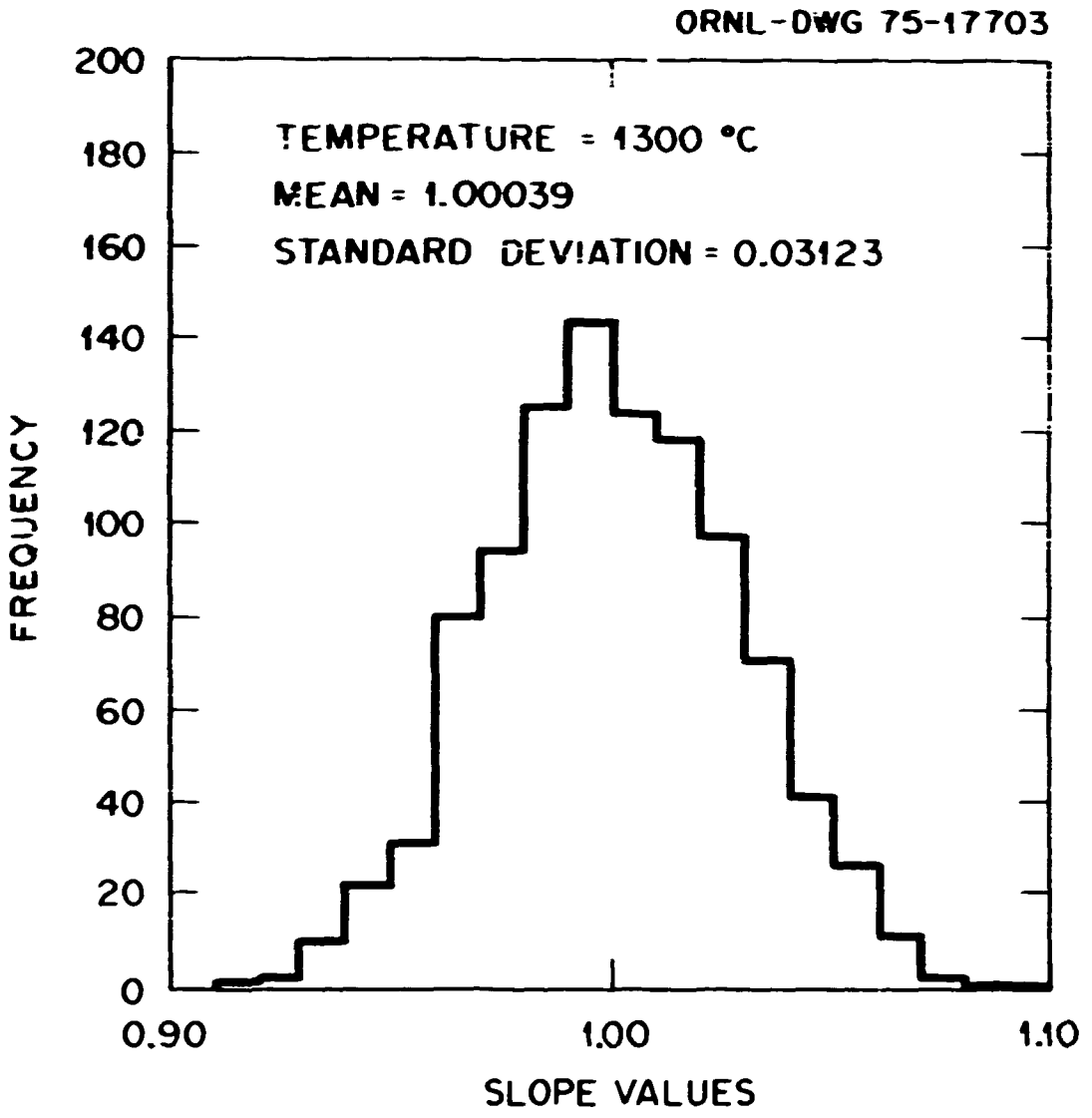

Fig. 15. Histogram of estimated slopes of oxidation rate curves calculated for 1300°C (2372°F).

slopes have values in the interval $1 \pm 2\sigma$, where σ is the standard deviation. The intervals containing 90, 95, and 99% of the data are shown in tabular form in Table 6.

Table 6. Intervals Which Contain Approximately 90%, 95%, and 99% of Simulated Slope Values

Temperature	90% Interval	95% Interval	99% Interval
900	0.92 – 1.08	0.90 – 1.10	0.86 – 1.14
1000°C	0.92 – 1.10	0.90 – 1.10	0.88 – 1.12
1100°C	0.94 – 1.08	0.92 – 1.08	0.90 – 1.10
1200°C	0.95 – 1.05	0.94 – 1.07	0.92 – 1.08
1300°C	0.96 – 1.05	0.95 – 1.06	0.93 – 1.07
1400°C	0.97 – 1.05	0.96 – 1.05	0.94 – 1.06
1500°C	0.96 – 1.03	0.96 – 1.04	0.94 – 1.05

Consider the first entry in the 90% interval at 900°C in the table. This result means that, given our experimental procedure and assuming a random temperature error of ±10°C (±18°F), there is a 90% probability that we will determine the rate constant to ±8% at 900°C (1652°F). The error predicted from Fig. 1 is ±15%. As might be expected, the anticipated error decreases with increasing temperature. Thus at 1500°C (2732°F) the predicted error range for the 90% confidence level is ~±3%.

This statistical treatment is presented not as a prediction of expected future results but rather as an indication of the extent to which the effects of random temperature errors can be minimized. It is unfortunately true that indeterminant temperature errors, especially, tend to be systematic rather than random, and it is obviously essential that every effort be made to insure the greatest possible accuracy in temperature measurements.

CONCLUSIONS

Accurate measurement of temperature in the experimental phase of the Zirconium Metal–Water Oxidation Program is essential. Through careful apparatus design and the use of well calibrated Pt vs Pt–10% Rh and Pt–6% Rh vs Pt–30% Rh thermocouples we have been able to achieve the following estimated uncertainties for the probable accuracy of temperature measurements in the three experimental apparatuses used.

1. MiniZWOK oxidation apparatus: ±4°C (7.2°F) at 900°C (1652°F) and ±6°C (10.8°F) at 1500°C (2732°F).
2. MaxiZWOK oxidation apparatus: same as above for isothermal experiments; for nonisothermal experiments there is an additional uncertainty estimated to reach ±5°C (9°F) in extreme situations.
3. Annealing Furnace: ±1°C (1.8°F) at 900°C (1652°F) and ±2°C (3.6°F) at 1500°C (2732°F).

The maximum possible error appears to be ~±10°C (18°F) for isothermal oxidation experiments and no more than ±4°C (7.2°F) for the annealing furnace.

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APPENDIX A

Calibration of Pt vs Pt–10% Rh (Type S) and Pt–6% Rh vs Pt–30% Rh Thermocouples from 25 to 1500°C (77–2732°F)

Five thermocouples were fabricated from Sigmund Cohn wire as indicated in Table 1. The wires were welded in an oxygen-acteylene flame, cleaned with acetone and alcohol and then annealed by electrical self-heating according to the following schedule: 1–2 min at 1400°C (2552°F), 15–30 min at 1200°C (2192°F), 1 hr at 1000°C (1832°F), and 2 hr at 500°C (932°F).

The annealed thermocouples were threaded into high purity, DeGussit AL-23 alumina insulators. For Run 1 thermocouples designated ZWOK-S1, S2, S3, and B1 were welded to the bead of the laboratory standard SL-7913. Run #2 included SL-7913, SL-7912, and ZWOK-S4 as indicated in Table 2. The assembly was inserted into a high purity, DeGussit AL-23 protection tube, open to the air, and this tube mounted in a furnace. The thermoelements were brought directly to reference junctions maintained at 0°C by crushed ice in a Dewar flask. Untinned copper leads (Western Electric telephone cable) were used to connect the thermoelements to the selector switch at the potentiometer. The selector switch was a silver alloy Leeds & Northrup switch. The switch was wired so that not only could the output of the individual thermocouples be read, but also the emf between the standard platinum thermoelement and the test platinum thermoelements as well as the emf between the test alloy thermoelements and the standard alloy thermoelement could be read. The emf's of the thermocouples were read using a Guildline 9930 DCC potentiometer. The data were recorded on paper tape for later computer processing.

The furnace was a tube-type furnace with a Pt-alloy heating element and was controlled by a Type S thermocouple attached to a CAT-type controller. The furnace power was supplied by an SCR-phase-fired power supply.

Table 1. Test Thermocouple Characteristics

Designation	Type	Wire Dia.	Material Identification
TWOK-S1	S	0.020 in. 0.020 in.	Pt, Bar 452, End a Pt-10% Rh, Bar 345, End a
TWOK-S2	S	0.020 in. 0.020 in.	Pt, Bar 452, End b Pt-10% Rh, Bar 345, End b
TWOK-S3	S	0.010 in. 0.010 in.	Pt, Bar 452, End a Pt-10% Rh, Bar 345, End a
TWOK-S4	S	0.010 in. 0.010 in.	Pt, Bar 452, End b Pt-10% Rh, Bar 345, End b
TWOK-B1	B	0.010 in. 0.010 in.	Pt-6% Rh, Lot No. 914 Pt-30% Rh, Lot No. 913

Table 2. Calibration Information

	Test Thermocouples		Standard Thermocouples	Max. Temp.	
	0.020 in. diam	0.010 in. diam		°C	°F
Run 1	S1, S2	S3, B1	SL 7913	1500	2732
Run 2		S4	SL 7913, SL 7912	1500	2732
Run 3	S1	New, Old	SL 7913, SL 7912	1000	2732

On the first run, the control thermocouple was located in the wall of the furnace. Above about 1000°C (1832°F), electrical leakage caused the measurements to be increasingly unstable, and at 1300°C (2372°F) the leakage increased to the point that reliable readings could not be made nor the furnace controlled. The furnace was cooled to room temperature, and an electrical shield for the alumina protection tube was made by winding a platinum wire on the alumina tube and connecting it outside the furnace to ground. At the same time the control thermocouple was transferred into the alumina protection tube. This seemed to solve the problems caused by electrical leakage. Tables 3 and 4 show the thermocouple and thermoelement comparisons for ZWOK S1 before the electrical leakage was corrected and for ZWOK S4 after the correction. The latter case shows agreement to better than 1.0 μV.

Table 3. Thermal Emf Comparisons in Microvolts for ZWOK S1 Thermocouple and Thermoelements to Reference SL 7913 Before Electrical Leakage Correction

Nominal Temperature °C	°F	Thermoelements Δ Pt Std.-Test	Δ Alloy Std.-Test	$\sum\Delta$(Pt − Alloy)	Thermocouple Δ EMF Std.-Test
25	77	0.1	0.6	−0.5	0.4
200	392	1.	0.6	1.3	1.2
400	752	1.9	0.2	1.7	2.3
600	1112	1.2	−2.6	3.8	3.9
700	1292	1.3	−2.8	4.1	4.3
800	1472	1.4	−3.3	4.7	4.8
900	1652	1.7	−3.6	5.3	5.4
1000	1832	2.0	−3.7	5.7	6.1
1100	2012	4.1	−2.3	6.4	7.6
1300	2372	−28.0	−41.5	13.5	9.5
1400[a]	2552	1.9	−8.1	10.0	10.6
1500[a]	2732	0.8	−8.5	9.3	10.2

[a]Measurements made after shielding installed.

Table 4. Thermal Emf Comparison in Microvolts for Zwok S4 Thermocouple and Thermoelements to Reference SL 7913 After Electrical Leakage Correction

Nominal Temperature °C	°F	Δ Pt Std.-Test	Thermoelements ΔAlloy Std.-Test	∑Δ(Pt − Alloy)	Thermocouple Δ EMF Std.-Test
25	77	0.1			−0.2
200	392	−0.3	−0.4	0.1	0
400	752	−0.7	−1.1	0.3	0.3
600	1112	−0.4	−0.9	0.5	0.5
700	1292	−0.5	−1.3	0.8	0.6
800	1472	−0.8	−1.5	0.7	0.9
900	1652	−0.6	−2.0	1.4	1.3
1000	1832	−0.3	−1.3	1.0	2.0
1100	2012	−0.2	−2.7	2.5	2.2
1200	2192	−0.2	−3.1	2.9	2.7
1300	2372	0.2	−3.4	3.6	3.4
1400	2552	1.0	−3.3	4.3	4.9
1500	2732	2.2	−3.4	5.6	4.7

Standards

The primary standard used in all runs was ORNL Type S standard SL-7913. In the second run, a mate to this thermocouple, SL-7912, was included, to check that SL-7913 had not been changed by the high temperature treatment in the first calibration run. The outputs of the two standard thermocouples agreed within 1 μV over the entire range of temperatures.

SL-7913 and SL-7912 are two thermocouples made from specially prepared wire acquired from Sigmund Cohn and given special calibrations

at the NBS; they were two of our six primary thermocouple temperature standards until the new Type S "exact" alloy was defined by NBS Monograph 125.* The voltage measurements were referenced directly through the Guildline potentiometer to one of the saturated standard cells used to maintain the value of the volt at ORNL.

Results

Tables and plots were calculated for each thermocouple using the ORNL thermocouple calibration program. These were referenced through SL-7913 and the Monograph 125* functions to IPTS-68. Figure 1 is a plot of the deviation of ZWOK-S1, ZWOK-S3, and ZWOK-S4 from the exact Type S thermocouple as a function of temperature. The average values for three thermocouples, ZWOK-AVE, was used to prepare a single table representing the ZWOK thermocouples. As Fig. 1 shows that the spread of these thermocouples amounts to about ±0.5°C. The line in Fig. 1 is least squares fit of the data to a third-degree polynomial. The behavior of ZWOK-S1 only is shown in Fig. 2. Thermocouple ZWOK-S2 was not included in the calculations of ZWOK-AVE because of somewhat more scatter in the data as shown in Fig. 3. This scatter is probably due to the electrical leakage observed at the 1100, 1200, and 1300°C (2012, 2192, and 2372°F) points, since the points at 1400°C and 1500°C (2552–2732°F) taken after installation of the shield wire agreed with the other two thermocouples in Run 1 run within about ±0.1°C (.18°F). It is not clear why ZWOK-S2 was affected by the leakage more than other thermocouples.

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*Robert L. Powell, William J. Hall, Clyde H. Hyink, Jr., Larry L. Sparks George W. Burns, Margaret G. Scroger, and Harmon H. Plumb, "Thermocouple Reference Tables Based on IPTS-68," NBS Monograph 125 (March 1974).

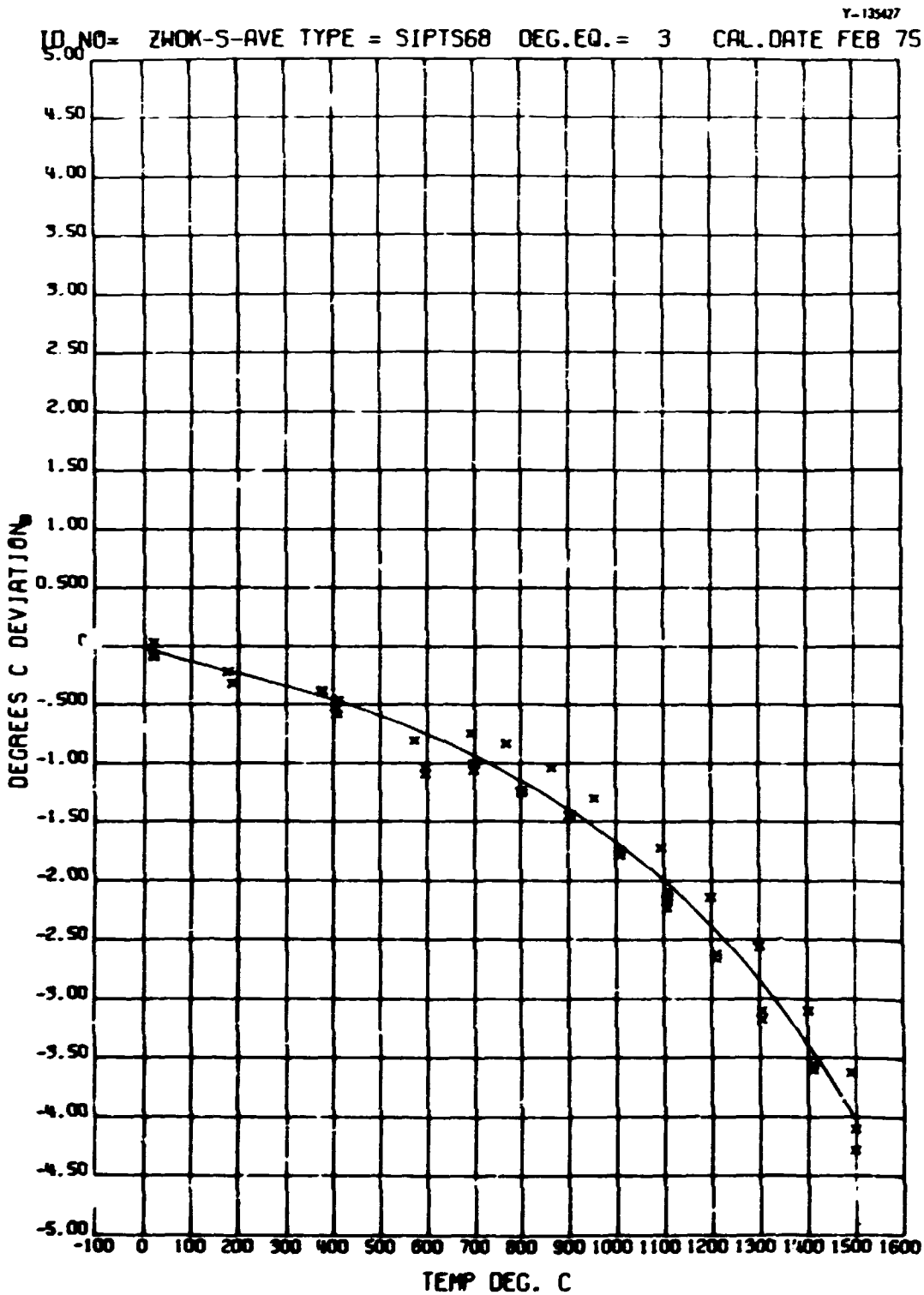

Fig. 1. Thermocouple deviation data for ZWOK S1, ZWOK S3, and ZWOK S4 from exact Type S thermocouple as a function of temperature.

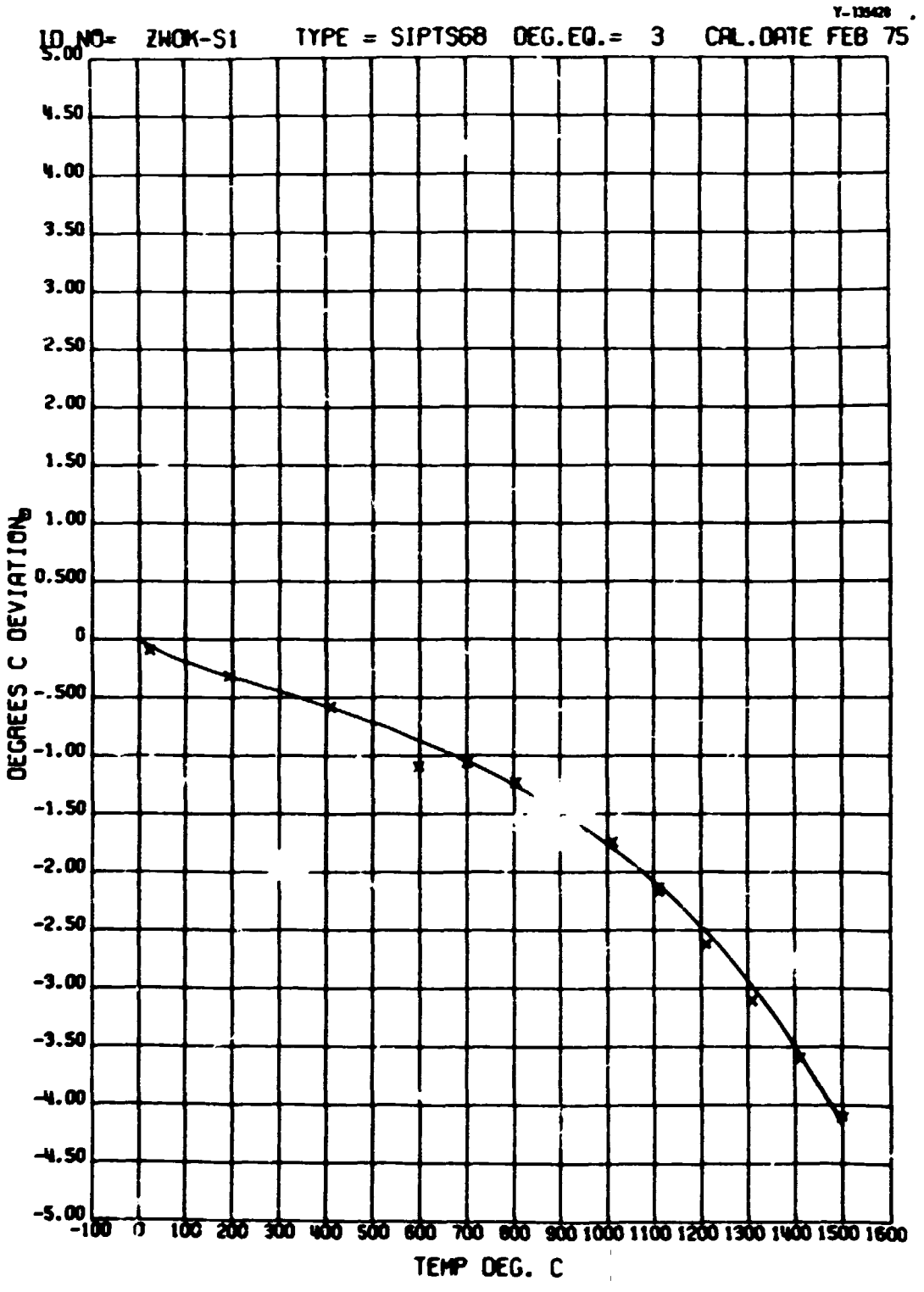

Fig. 2. Thermocouple deviation data for ZWOK S1 from an exact Type S thermocouple as a function of temperature.

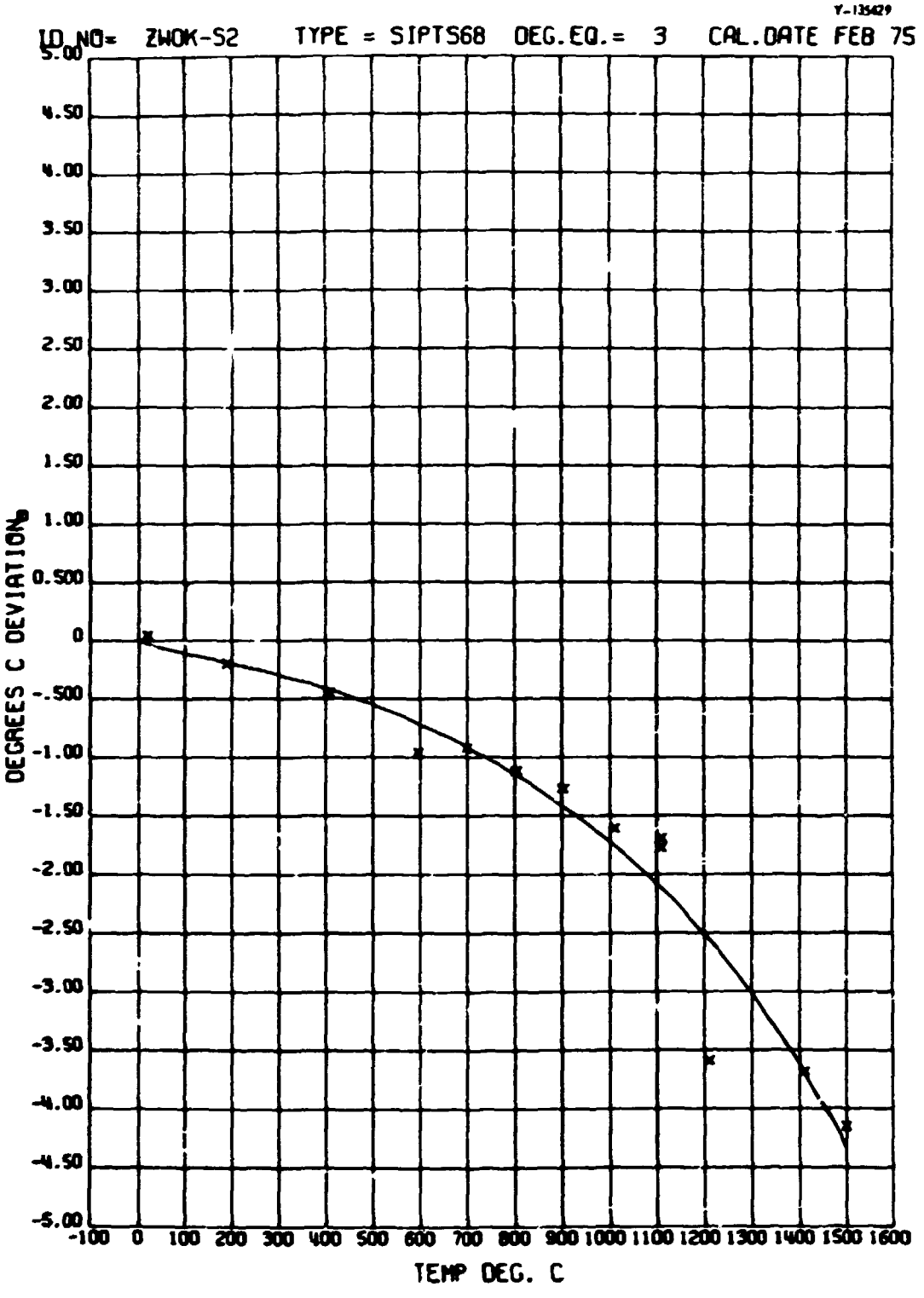

Fig. 3. Thermocouple deviation data for ZWOK S2 from an exact Type S thermocouple as a function of temperature.

The data in run #1 were taken in the order:

Emf - Std. SL-7913
ZWOK-S1
ZWOK-S2
ZWOK-S3
ZWOK-B1
Std. SL-7913

Pt-Std. vs Pt-test
ZWOK-S1
ZWOK-S2
ZWOK-S3
ZWOK-B1

Alloy-Std. vs Alloy-test
ZWOK-S1
ZWOK-S2
ZWOK-S3
ZWOK-B1

Emf-Std. SL-7913

Maintaining this measurement schedule, allows one to use the behavior of SL-7913 to correct for furnace temperature drift at a given calibration temperature.

At a given temperature a linear drift of the furnace was assumed and the test emf's were adjusted accordingly. Table 5 gives the maximum differences observed between the two standard emf measurements at the various test temperatures.

Figure 4 is a reproduction of page 1 of the calibration table for ZWOK-S-AVE for the range 0 to 49°C (32–120°F) in one degree steps. Entries in this table include the thermal emf (millivolts) at each temperature as well as the temperature derivative (millivolts per degree) to allow interpolation. The complete table extended from 0 to 1499°C (32–2730°F).

Thermocouple ZWOK-B1, Pt–6% Rh vs Pt–30% Rh, was included in Run #, and Fig. 5 compares its behavior to that reported in Monograph 125.[1] Except for the data scatter at 1100 and 1200°C (2012–2192°F) associated with electrical leakage, the calibration appears quite acceptable and a table similar to Fig. 4 was prepared for this combination.

Y-135430

ID NO = ZWOK-S-AVE TYPE = SIPTS68 CAL.DATE = FEB 75 PAGE 1

DIFFERENCE TABLE-DEG.EQ.= 3

TEMPERATURE = DEG C(INT)
VOLTAGE = MILLIVOLTS(ABS)

TEMP		TEMP		TEMP		TEMP		TEMP	
0	0.0 0.00540	10	0.05513 0.00565	20	0.11263 0.00588	30	0.17238 0.00609	40	0.23425 0.00630
1	0.00540 0.00543	11	0.06077 0.00567	21	0.11850 0.00590	.	0.17847 0.00612	41	0.24056 0.00632
2	0.01083 0.00545	12	0.06644 0.00569	22	0.12440 0.00592	32	0.18458 0.00614	42	0.24688 0.00634
3	0.01628 0.00548	13	0.07213 0.00572	23	0.13032 0.00594	33	0.19072 0.00616	43	0.25322 0.00636
4	0.02176 0.00550	14	0.07785 0.00574	24	0.13626 0.00596	34	0.19688 0.00618	44	0.25958 0.00638
5	0.02726 0.00553	15	0.08359 0.00576	25	0.14223 0.00599	35	0.20306 0.00620	45	0.26596 0.00640
6	0.03278 0.00555	16	0.08935 0.00579	26	0.14821 0.00601	36	0.20925 0.00622	46	0.27236 0.00642
7	0.03833 0.00557	17	0.09514 0.00581	27	0.15422 0.00603	37	0.21547 0.00624	47	0.27878 0.00644
8	0.04391 0.00560	18	0.10094 0.00583	28	0.16025 0.00605	38	0.22171 0.00626	48	0.28522 0.00646
9	0.04951 0.00562	19	0.10677 0.00585	29	0.16630 0.00607	39	0.22797 0.00628	49	0.29167 0.00648

Fig. 4. Page 1 of calibration table for ZWOK-S-AVE thermocouple.

Table 5. Linear Drift used in Calibrations

Test Temperature °C	°F	Drift (μV)
21.45	70.61	0.3
192	378	0.2
409	768	1.3
598.5	1109.3	0.2
701	1294	1.7
804	1472	0.4
904	1659	1.5
999	1830	2.0
1109	2028	4.5
1308	2386	2.3
1412	2574	4.1
1500	2732	3.2

Retest of 0.010 in. Type S Material (Run 3)

A sample of a used 0.010 in Type S thermocouple (old) was submitted for retest along with a new thermocouple (new), both made from the same materials previously calibrated. The calibration was run in a similar manner to that previously described, but the temperature range extended to only 1000°C. Data were taken both on heating and on cooling. Figures 6 and 7 show that no substantial difference was found between the "new" and the "old". Both were within ±0.5°C (0.9°F) of the ZWOK-S1 thermocouple which was included as a reference along with laboratory standard SL-7913. SL-7913 was the same reference standard used in the first ZWOK calibration run.

R. L. Anderson
Metrology Research & Development
Laboratory
Report of Calibration
November 24, 1975

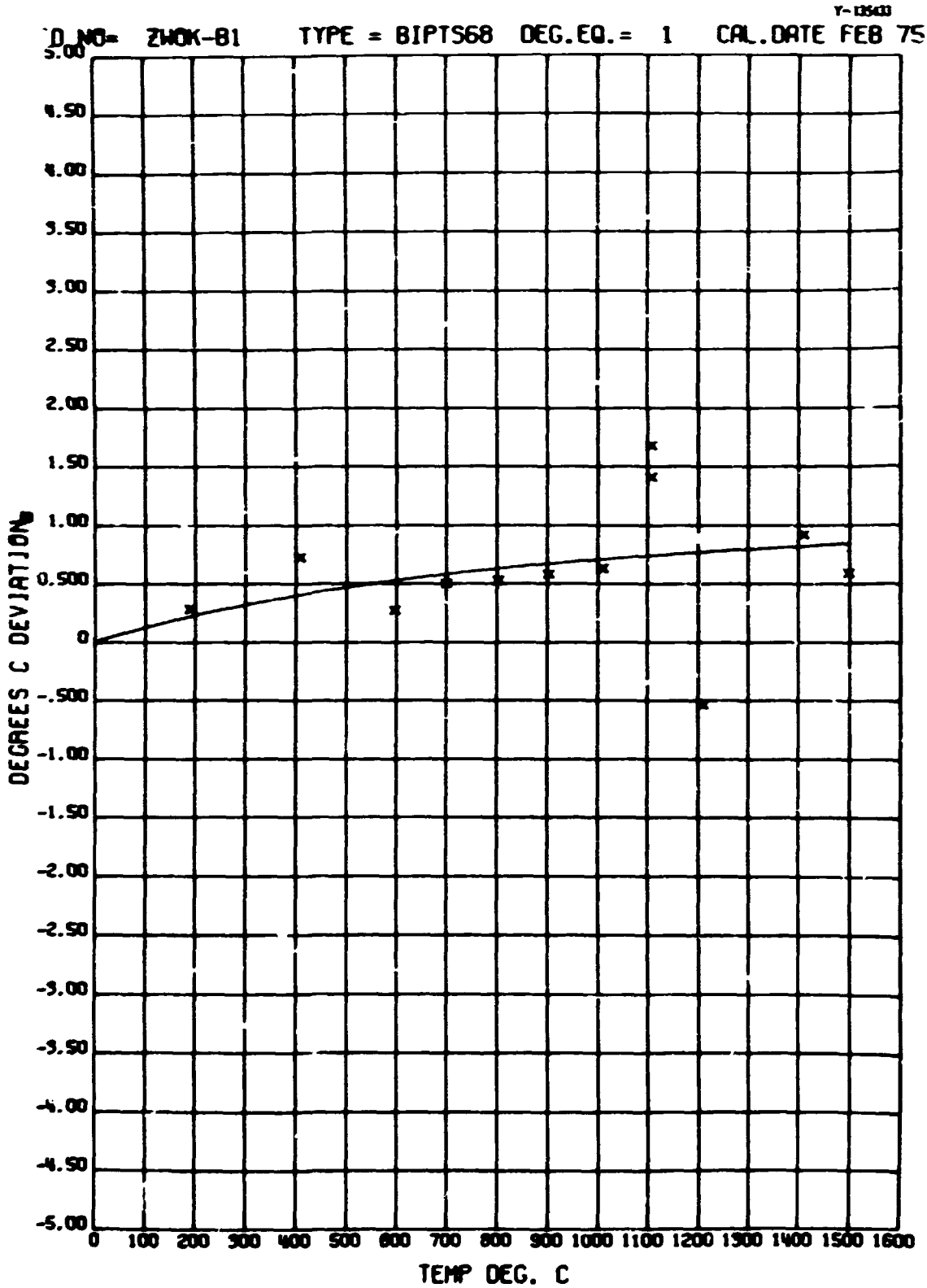

Fig. 5. Thermocouple deviation data for ZWOK B1 from NBS monograph 125 as a function of temperature.

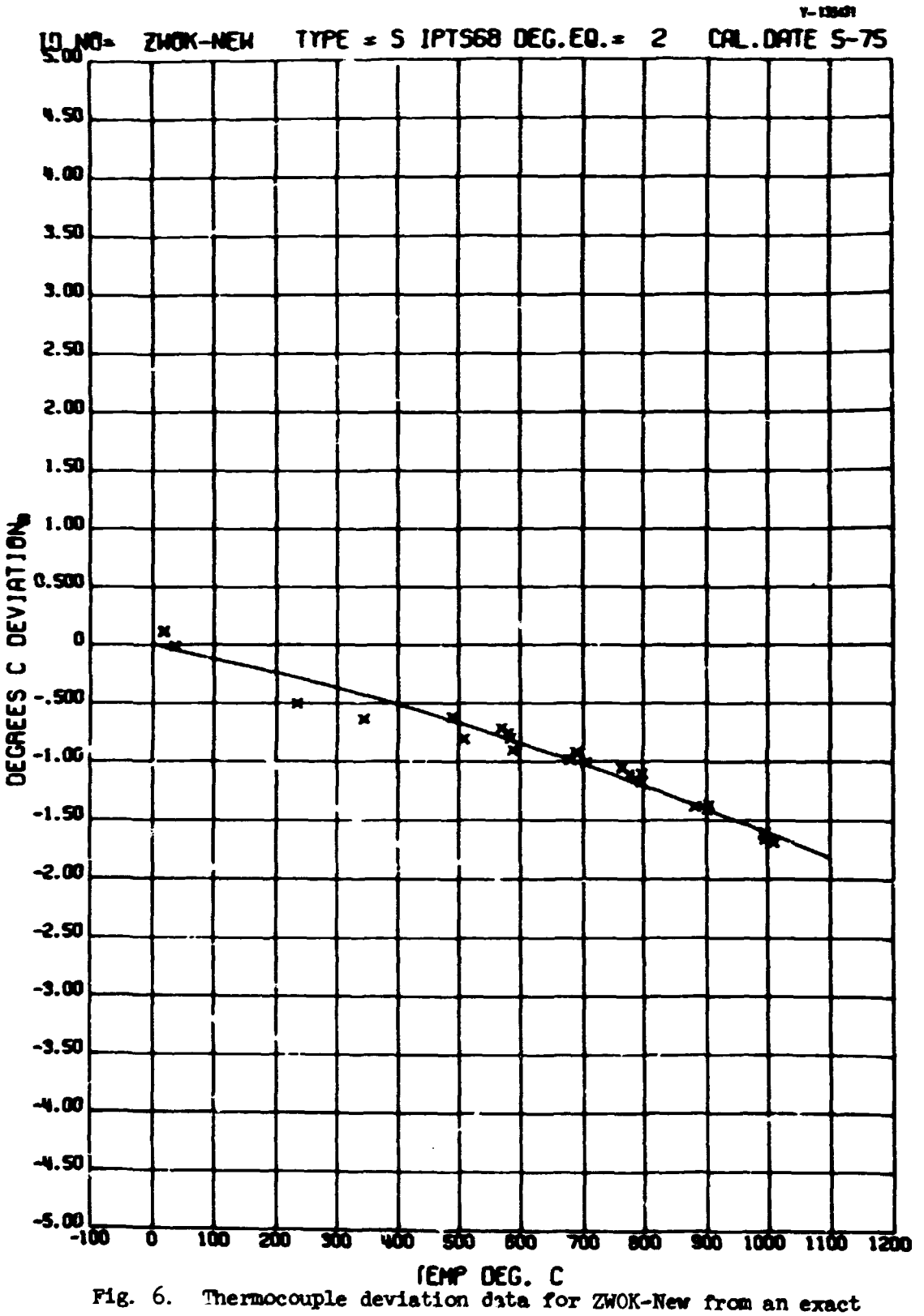

Fig. 6. Thermocouple deviation data for ZWOK-New from an exact Type S thermocouple as a function of temperature.

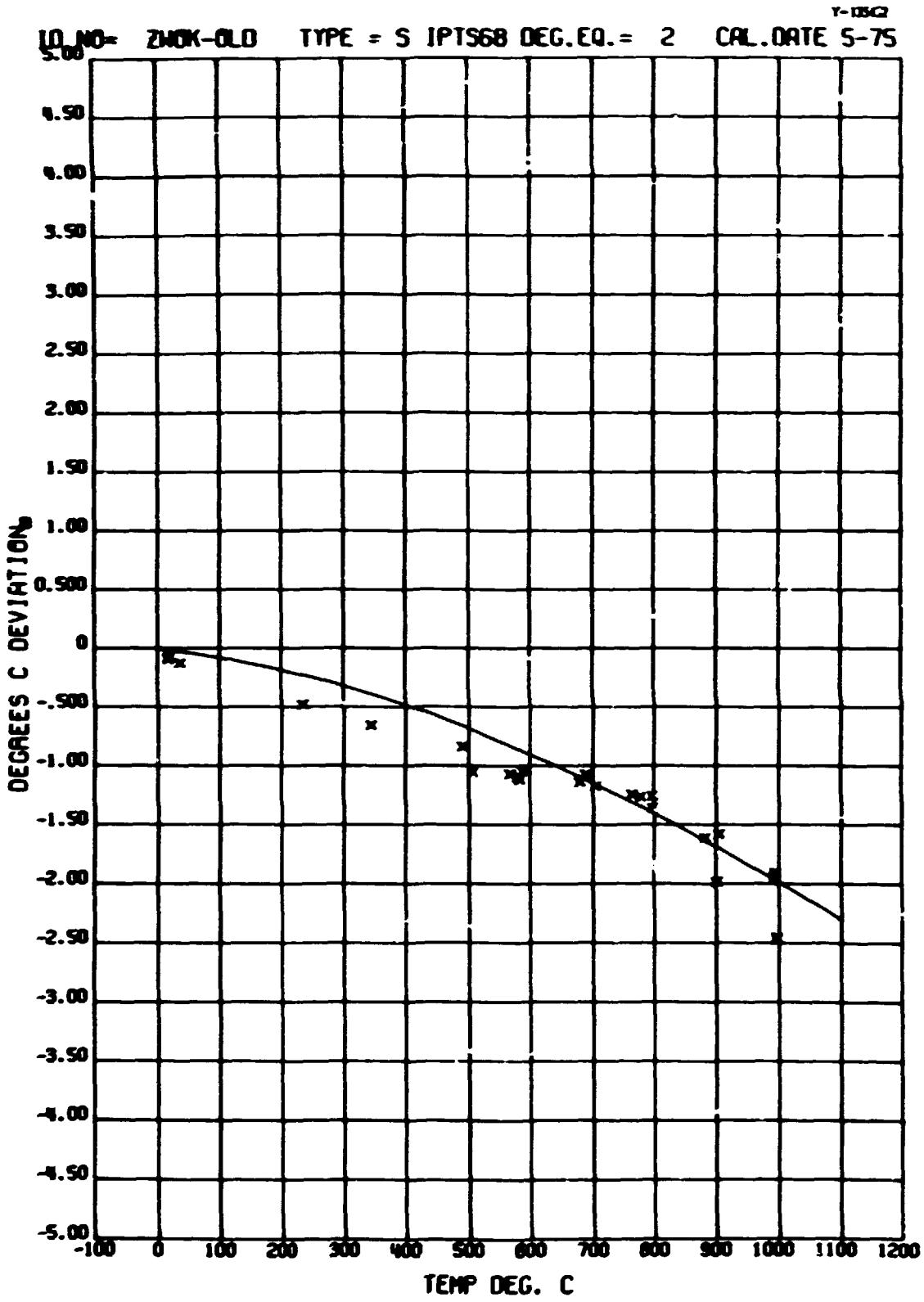

Fig. 7. Thermocouple deviation data for ZWOK-Old from an exact Type S thermocouple as a function of temperature.

APPENDIX B

Reference Junction Systems

The Pt–10% Rh, Pt, Pt–30% Rh and Pt–6% Rh wires for each of the thermocouples of the experimental systems (MiniZWOK, MaxiZWOK, and the annealing furnace) were individually joined by mechanically twisting to vinyl-insulated copper telephone wires to form the cold junctions. These cold junctions were insulated from each other by vinyl tubing and were placed two each in 7 mm (0.28 in.) diam glass tubes 25 cm (10 in.) long partially filled with a ~10 cm (4 in.) long column of mineral oil for thermal uniformity. A silastic compound was extruded into the open end of each glass tube to seal the cold junction to minimize water accumulation in the tubes. This procedure precludes electrical shunting between the cold junction wires.

The sealed glass tubes were mounted in a cork stopper which formed the top of a Dewar flask containing the 0°C (32°F) ice water bath. Good thermal contact of the cold junctions with the bath was assured by the large L/D ratio of the tubes (~36) and the mineral oil column. Previous experiments have shown that similarly constructed cold junctions obtain the bath temperature at a depth of immersion of less than 10 cm (4 in.).* Various combinations of water and ice formed from distilled and tap water obtain 0°C well within the ±0.01°C limit specified in the foregoing error analysis.† The cold junction used in the Metrology Laboratory thermocouple calibration facility was of a similar design, and the thermal EMFs associated with the copper wire circuit were found to be 0.015 microvolts (~0.003°C).

In the annealing furnace cold junction system the glass tubes were fitted in a drilled copper block which was immersed in the bath. This copper block provided further insurance that all of the cold junctions

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*D. L. McElroy, Progress Report 1, Thermocouple Research Report for the Period November 1, 1956 to October 31, 1957, ORNL-2467 (March 1958).

†J. P. Moore, R. S. Graves, T. G. Stradley, J. H. Hannah, and D. L. McElroy, Some Thermal Transport Properties of a Limestone Concrete, ORNL-TM-2644 (August 1969).

were at the same temperature and served as a thermal inertia block in maintaining the cold junction temperature constant during the time the ice bath was being changed. This was useful in long time diffusion anneals to prevent major changes in the control of the furnace temperature due to bath replenishment.