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# Argonne National Laboratory

## CHEMICAL ENGINEERING DIVISION
## SUMMARY REPORT

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# STUDIES OF METAL-WATER REACTIONS AT HIGH TEMPERATURES:
## I. THE CONDENSER DISCHARGE EXPERIMENT: PRELIMINARY RESULTS WITH ZIRCONIUM

by

L. Baker, Jr., R. L. Warchal, R. C. Vogel, and M. Kilpatrick

Chemical Engineering Division

May 1961

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# STUDIES OF METAL-WATER REACTIONS AT HIGH TEMPERATURES: I. THE CONDENSER DISCHARGE EXPERIMENT: PRELIMINARY RESULTS WITH ZIRCONIUM

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L. Baker, Jr., R. L. Warchal, R. C. Vogel, and M. Kilpatrick

## I. ABSTRACT

The condenser-discharge method of conducting molten metal-water reactions at high temperatures was refined. Two methods to measure energy input to specimen wires and, therefore, to compute initial metal temperatures were developed. Calculated metal temperatures were estimated to be accurate to within 100 C. Two reaction cells were designed, one for operation at atmospheric pressure with water at room temperature, and the other for operation at high pressure and with water at elevated temperature. Means were developed to determine the surface area of metal exposed to reaction and to determine the total extent of reaction. Pressure transducers were used to record the rate of reactions.

The zirconium-water reaction was studied with initial metal temperatures from 1100 to 4000 C with 30 and 60-mil wires in room-temperature water. Initial pressures in these runs were the vapor pressures of water at room temperature (20-30 mm). Runs were made with 60-mil wires in water heated to 200 C (225 psi). Results in room-temperature water indicated that the reaction became explosive at an initial metal temperature of 2600 C. Below this temperature, 20% or less reaction occurred. At higher water temperatures, reaction ranged from 40 to 70%. Runs in heated water showed markedly greater reaction, reaching 50% for fully melted metal at the melting point (1840 C). Results suggested that the rates of both solid-state processes and the diffusion of water vapor through the hydrogen blanket surrounding reacting particles must be considered.

## II. INTRODUCTION

There has been great interest in recent years in methods to study reaction between molten metals and water at very high temperatures.(1-29) This interest stems from the additional heat liberation possible by means of such reactions during an accident in a nuclear reactor. A coolant failure or a severe nuclear excursion could conceivably cause melting and even vaporization of the core of a water-cooled reactor. This could explode a mixture of solid, liquid, and vaporized metal into the cooling water.

Thermodynamic data show that most of the metals commonly used in reactor cores (uranium, zirconium, aluminum, and stainless steel) have the potential to react with water with the liberation of considerable heat and hydrogen gas. The amount of energy released by such a reaction could be comparable to that released by the fission process during a nuclear runaway.

Calculations based on the Borax I reactor may be used to illustrate the importance of metal-water reactions. The final destructive Borax I burst was estimated to have liberated 135 megawatt-seconds, or 32,260 kilocalories, of fission energy.(30) This energy is compared in the following tabulation with the additional energy release that would have occurred if either 10 or 50 percent of the aluminum present in the reactor had undergone a metal-water reaction. Calculations are included for a hypothetical reactor having dimensions identical with those of Borax I. The fuel cladding and the structural elements of the hypothetical reactor are zirconium instead of aluminum. The volume of hydrogen generated by the metal-water reaction and the heat released by subsequent combustion of the hydrogen with air are also tabulated.

| Reactor | Borax I | Hypothetical Reactor |
|---|---|---|
| Cladding Metal | Aluminum | Zirconium |
| Volume of Metal, $cm^3$ | 46,770 | 46,770 |
| Weight of Metal, kg | 126.3 | 304.0 |
| Fission Energy Released by Destructive Transient, kcal | 32,260 | 32,260 |
| 10% Metal-Water Reaction | | |
| Chemical Energy Release, kcal | 146,600 | 48,600 |
| Volume $H_2$ Generated, liters STP | 15,700 | 14,900 |
| Heat of $H_2$ Combustion, kcal | 40,600 | 38,600 |
| 50% Metal-Water Reaction | | |
| Chemical Energy Release, kcal | 733,000 | 243,000 |
| Volume $H_2$ Generated, liters, STP | 78,500 | 74,500 |
| Heat of $H_2$ Combustion, kcal | 203,000 | 193,000 |

It is evident from the calculations that even a 10 percent metal-water reaction might contribute more energy toward a disaster than the fission process.

The economic design of a containment shell surrounding a water-cooled reactor then requires precise knowledge of the rates of metal-water reactions at high temperatures. It is particularly important to find out what conditions, if any, could lead to a rapid self-sustained reaction which could cause blast loadings on the containment vessel.

This paper describes the use of the condenser-discharge experiment to investigate metal-water reactions at high temperature. Experimental results are given for the zirconium-water reaction. The detailed mechanism of the reaction will be considered in a later paper.

## III. PREVIOUS EXPERIMENTAL METHODS

Molten metal-water reactions are in the category of rapid chemical reactions. The most critical requirement of an experimental method to determine rates of rapid reactions is that the reactants must be brought together at the reaction temperature in a time which is short compared to the period of observation. It is often impossible to carry out rapid reactions under isothermal conditions. This is because it is not possible to supply or remove heat at a great enough rate. Fortunately, methods for dealing with nonisothermal reactions are available. Frank-Kamenetskii(31) and others have shown how the effects of self-heating and external cooling of a reaction mixture may be treated. Their work has shown how critical conditions such as ignition or other abrupt changes in the apparent reaction rate may be explained in terms of the fundamental parameters of the rate equations and the transport properties of the system.

Molten metal-water reactions are heterogeneous, so that the control of interfacial area must also receive important consideration. The experimental methods that have been used to study metal-water reactions involved either the rapid contacting of heated metal with water or the rapid heating of metal already in contact with water. In many cases, the heating or contacting was too slow and significant reaction occurred under uncontrolled conditions. The experimental methods that have been used to study metal-water reactions can be divided into six broad categories as follows:

### A. Rapid Contacting Methods

1. Pouring or spraying metal into water
2. Molten metal drops falling into water
3. Dispersion of molten metal by an explosive charge

### B. Rapid Heating Methods

4. Inductive heating of metal immersed in water or steam
5. In-pile heating in MTR
6. Heating and dispersion of metal by a condenser discharge

A more detailed outline of the methods used by previous investigators and a summary of their results were prepared by the authors before beginning studies by the condenser-discharge method. This material was then edited by R. O. Brittan and included in a comprehensive discussion of reactor containment.(32) This outline has been further edited and is repeated in Appendix A. Several investigations have been carried out since this survey was made, and these investigations are cited by reference only and not further discussed.

The rapid contacting methods involved complicated apparatus and were generally limited in the range of temperature available for study and in means of following the reaction. Methods involving rapid heating were limited by the time required to heat and by the control and measurement of interfacial area. The only method affording a satisfactory heating rate was the condenser-discharge method. Heating of metal by a condenser discharge offered the possibility of heating to virtually any temperature from a few microseconds up to many milliseconds. With very slow heating rates, however, it is generally not possible to exceed the melting point, because the metal wire has time to part before the current surge can be completed.

Condenser discharges through wires have been used to produce high-intensity light flashes, magnetic fields, shock waves, plasmas, colloidal dispersions of metals in fluids, and as a means of studying metal-water reactions. Very recent studies of wires exploded by surge currents from discharging condensers have led to a limited understanding of the process.(33) In general, the current in a circuit consisting of a condenser shorted through a fine wire will begin to rise rapidly. Joulean heating will bring the metal through the melting point, producing liquid metal. The physical shape of the wire is maintained principally by inertia and to some extent by magnetic forces. Heat addition continues to increase the metal temperature until well above the normal boiling point. Boiling begins to occur only after considerable superheating and occurs with explosive violence. At first there is a continuous phase of liquid interspersed with vapor at high pressure. Further heating leads to a continuous vapor phase interspersed with liquid droplets. The authors refer to the violent conversion from liquid metal interspersed with vapor to vapor interspersed with liquid as a transplosion.(33) The high-pressure metal vapor is a poor conductor of electricity so that there is a dramatic current cut-off at the time of transplosion. The high-pressure vapor expands in the form of a shock wave until the pressure is low enough (higher mean free path) to permit ionization by impact between electrons and metal atoms. At this point, current can again build up to a large value by the avalanching that attends ionization by impact. The remaining energy stored in the condenser is then discharged into the arc.

It would appear from this model of an electrically exploded wire that uniformly heated metal can be prepared up to temperatures of the order of the normal boiling point of the metal. The transplosion and the production of an arc can be prevented by limiting the energy stored in the condensers initially. The only quantitative metal-water data that have been obtained previously using the condenser-discharge method were those of Reubsamen, Shon, and Chrisney.(26) They obtained the extent of reaction as a function of energy input to the wire for several metals. Their method of estimating the energy input to the wire was very approximate. They estimated a ratio between the resistance of the wire to be heated and the stray resistance in the condensers and the circuitry. They used this ratio to calculate the fraction of the total stored energy that actually went into the wire. They ignored the fact that the resistance of the specimen wire changes drastically during the heating. Their results showed that a high percentage of reaction occurred between several metals and water but that no self-sustained reactions were initiated that would cause complete reaction.

## IV. EXPERIMENTAL

### A. The Discharge Circuit

The basic circuit of the condenser discharge experiment is shown in Figure 1. An alternative circuit including a resistive element shunting the specimen wire was also used. The shunting path is shown by the dotted lines in Figure 1. The condensers C are charged by a separate source of high voltage. A spark gap similar to one described by Cullington(34) was used to initiate the discharge. A 15,000-volt pulse on the ignition electrode rendered the spark gap conducting and also triggered several oscilloscope sweeps.

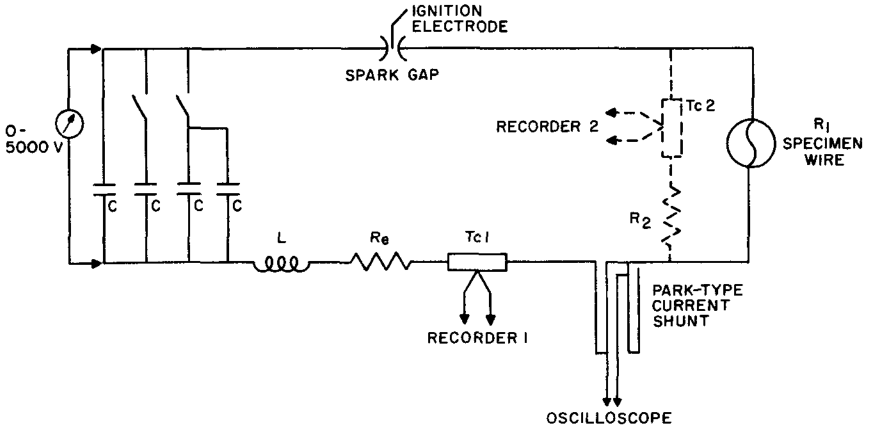


FIGURE I
BASIC CIRCUIT OF CONDENSER–DISCHARGE METHOD

C - CONDENSER (25 $\mu$f, 7000 V)
L - CIRCUIT INDUCTANCE
$R_e$ - EXTRANEOUS CIRCUIT RESISTANCE
Tc - THERMOCOUPLE ELEMENTS

## 1. Energy Storage

The total energy E stored in a condenser depends on the capacitance C and the charging voltage V as follows:

$$E = \frac{1}{2} CV^2 \quad .$$

It was decided at the outset of the program to use the minimum voltage consistent with adequate energy storage. A maximum charging voltage of 5000 volts was arbitrarily selected. This reduced the tendency toward stray arcing between adjacent circuit elements. A total of four condensers of nominal 25-$\mu$farad capacitance and 7000 working volts were arranged so that either one, two, or all four could be connected in parallel. The capacitance of each combination was determined by measurements of the current-time oscillogram obtained by discharging through a calibrated 100-ohm resistor. The following values were calculated for the energy stored at 5000 volts:

| Number of Condensers | Total Capacitance, $\mu$farad | Energy Stored at 5000 volts, $E_{5000}$, cal |
|---|---|---|
| 1 | 24.8 | 74 |
| 2 | 49.5 | 148 |
| 4 | 99.0 | 296 |

## 2. Measurement of Discharge Current and Heating Time

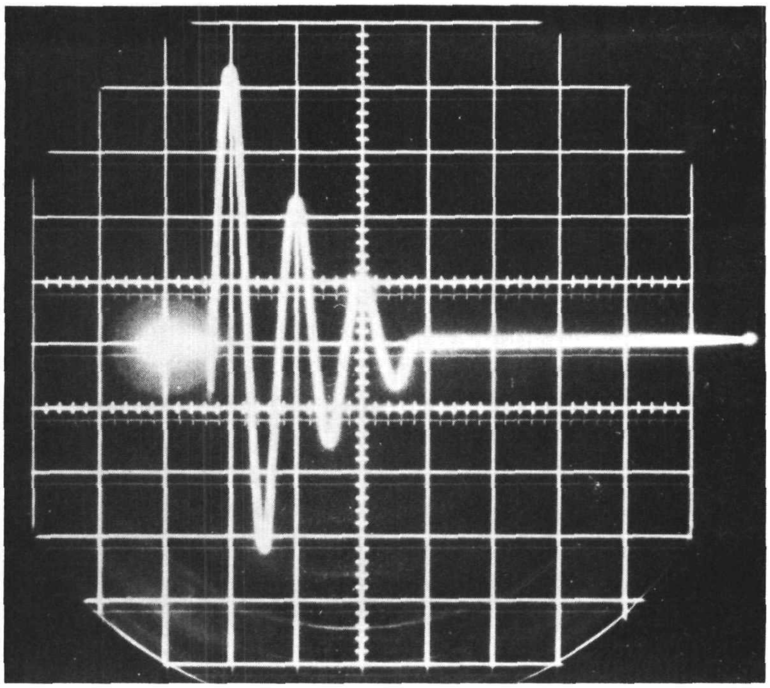
The experiment was designed to heat as much metal as possible so that the resistances of the specimen wires were very small. The extraneous circuit resistance, therefore, had to be kept to an absolute minimum. It was not feasible, however, to locate the condensers and circuitry immediately adjacent to the reaction cell containing the specimen; thus, fairly long lead wires were used. This led to a relatively large circuit inductance, although the lead resistance was kept low by using massive copper leads. The high circuit inductance was thought to be desirable because it prevented extremely high currents and rapid current changes, thus avoiding excessive magnetic and skin effects. At the same time, the heating rate remained rapid by conventional standards of chemical kinetics. The transient current is shown in Appendix B to have the form of a damped oscillation under conditions of low circuit resistance.

The current was measured experimentally by means of coaxial shunt (see Figure 1) of the type devised by Park.(35) It was constructed entirely of copper tubing. The voltage leads were connected to the vertical plates of a cathode ray oscilloscope. Current-time curves were recorded by means of a Polaroid Oscilloscope Camera. A typical oscillogram is reproduced in Figure 2. The total circuit inductance can be obtained from an analysis of the current oscillogram, as outlined in Appendix B. A value of 2.5 $\mu$henry was consistently obtained. It was then possible to calculate a current-time curve from electrical theory using the value of inductance and values of circuit resistance calculated by methods to be described later. Calculations indicated that the oscillations should continue indefinitely with a continuously decreasing amplitude. In practice, the spark gap fails to reignite as the current passes through zero after most of the energy has been dissipated. This gives a well-defined current cut-off and allows a precise statement of the heating time for a given run.

Figure 2

CURRENT OSCILLOGRAM OF A DISCHARGE THROUGH
A 64-MIL NICHROME WIRE

Length, 1.09 in.
Total Capacitance, 99 $\mu$farad
Charging Voltage, 2500
[a]Ordinate, 2700 amp/cm
[a]Abscissa, 0.10 msec/cm



[a] The spacing between grid lines on all oscillograms is one cm at the face of the cathode ray tube.

Several important features are shown in Appendix B to result from operation with a relatively high inductance. The oscillation frequency and the peak current are relatively independent of the specimen resistance.

The specimen resistance normally changes markedly during a discharge. The frequency of oscillation depends only on the number of condensers used and has the following values:

| Number of Condensers | Frequency, $\text{sec}^{-1}$ | Period of Half Cycle, msec |
|---|---|---|
| 1 | 20,000 | 0.025 |
| 2 | 14,000 | 0.035 |
| 4 | 10,000 | 0.050 |

The heating time is an integral number of half cycles. The number depends strongly on the specimen resistance, increasing with decreasing resistance. Heating time varies from 0.15 msec for a typical high-resistance specimen to 0.45 msec when the specimen wire is replaced by a heavy copper shorting bar. Nominal heating time was taken to be 0.3 msec.

Some energy normally remains in the condensers following a discharge because of the cut-off characteristic of the spark gap. The residual energy does not exceed 0.5% of the original energy and was, therefore, ignored.

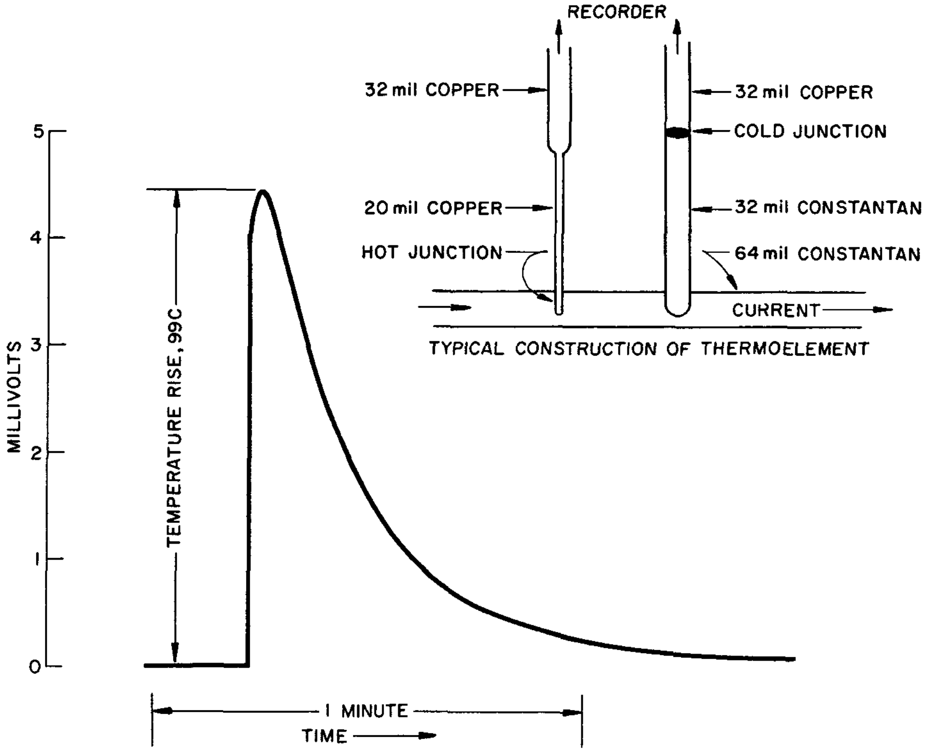
### 3. Energy-measurement Methods

The energy imparted to the specimen wire during a discharge is the most important parameter to be measured. The energy given to the specimen differs considerably from the energy initially stored in the condensers. This results from the fact that the resistance of the extraneous circuitry, $R_e$ in Figure 1, cannot be made small compared with the specimen resistance. This could be done only if one were interested exclusively in very fine specimen wires. The extraneous resistance includes the effective resistance of the spark gap, the internal resistance of the condensers, and the lead resistance.

Two methods of measuring the energy distribution within the circuit were devised. The first method is more generally applicable if, for example, more rapid discharges were to be employed. The second method is, however, more accurate for the low-frequency oscillatory discharges employed in the present study.

Both methods rely on the use of small circuit elements consisting of short lengths of carefully sized constantan wires with fine copper wires soldered to their outer surface. In the first method to be described, only one such element is used (Tc 1 in Figure 1); in the second method, two are used. The constantan wires are heated by the discharge current along with the specimen wire. The constantan wires are sized so that the most powerful discharges to be used will result in a temperature rise of 200 C or less. The fine copper wire and an additional constantan lead are connected to a millivolt recorder of moderately high speed.* A typical chart record of a discharge and the dimensions of a typical thermocouple element are shown in Figure 3. The peak recorder reading is taken to represent approximately the total temperature rise experienced by the constantan wire and is not meant to represent the rate of temperature rise, as the recorder clearly does not follow the heating. The relatively slow rise during the final 10 degrees before the peak in Figure 3 is thought due to thermal equilibration between the constantan and the thermocouple bead. The decrease following the peak is due to cooling in air.

FIGURE 3
TYPICAL CHART RECORD OF A DISCHARGE



In the general case, the energy generated per unit length of wire is

$$\int_0^\infty R_c i^2 dt \quad , \tag{1}$$

where $R_c$ is the resistance per unit length, i is instantaneous current, and t is time of current flow. The resistivity of constantan is nearly independent

---

*A Brown Instruments Recorder 0-10 mv, $\frac{1}{4}$-sec pen speed, 4-in./min chart speed was found to be very suitable.

of temperature over the range considered, so that $R_c$ can be taken out of the integral. The energy absorbed per unit length is also expressible in terms of temperature rise:

$$C_p \rho_A \, \Delta T = R_c \int_0^\infty i^2 \, dt \quad , \tag{2}$$

where $C_p$ is specific heat, $\rho$ is density, A is cross-sectional area of wire, and $\Delta T$ is temperature rise. Rearranging and grouping constants,

$$\Delta T = k \int_0^\infty i^2 \, dt = kS \quad , \tag{3}$$

where k is $R_c/C_p \rho_A$ and S is $\int_0^\infty i^2 \, dt$. The temperature rise is shown in Equation 3 to be proportional to the total "action integral," S, used by recent investigators to correlate data during studies of exploding wires.(33) The action integral when multiplied by the resistance of any series circuit element gives the energy absorbed by that element.

### a. Energy-measurement Method I

In this case, only one thermocouple element, connected in series with the specimen wire in the discharge circuit, is used. The total energy involved in a discharge is divided between the specimen and the extraneous resistance as follows:

$$E_{\text{Total, Run}} = \frac{1}{2} C V_R^2 = E_1 + R_e S \quad , \tag{4}$$

where $V_R$ is the charging voltage used in the run, $E_1$ is the energy absorbed by the specimen wire, and $R_e$ is the extraneous circuit resistance. The energy $E_1$ can be obtained by conducting a series of calibration discharges with the specimen replaced by a heavy shorting bar. Under these conditions, negligible energy is absorbed by the shorting bar:

$$E_{\text{Total, Cal}} = \frac{1}{2} C V_c^2 = R_e S \quad , \tag{5}$$

where $V_c$ is the charging voltage used in a calibrating discharge. Subtracting Equation 4 from Equation 5 yields

$$E_1 = \frac{1}{2} C V_R^2 - \frac{1}{2} C V_c^2 \quad . \tag{6}$$

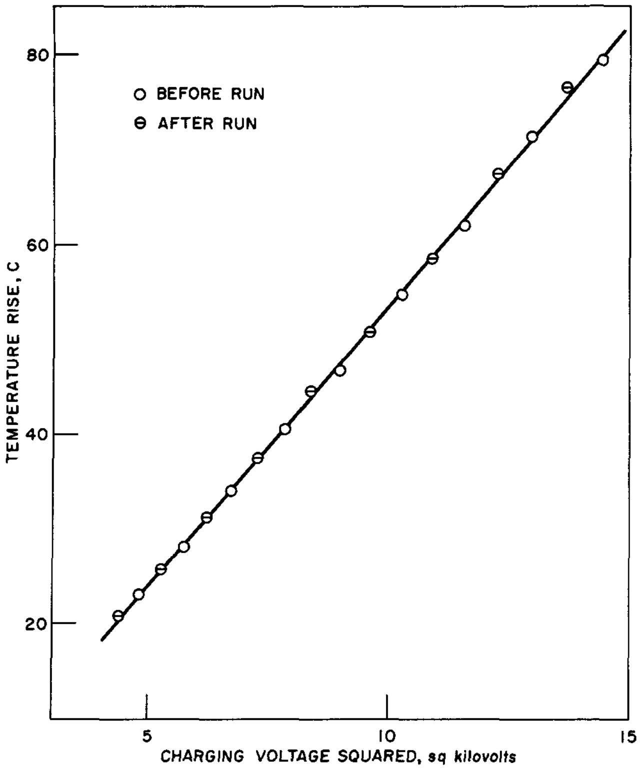
Equation 6 applies so long as the same action integral obtains in both discharges. This is accomplished in practice by preparing a calibration plot.

Equations 3 and 5 can be combined to yield

$$\Delta T = \frac{kC}{2R_e} V_c^2 \quad . \tag{7}$$

A typical plot of $\Delta T$ vs $V_c^2$ is shown in Figure 4 to be approximately a straight line, as required by Equation 7. The method of computing the energy absorbed by a specimen during a discharge of charging voltage $V_R$ is to find the $V_c^2$ from the plot using the $\Delta T$ found for the run. Equation 6 is then used to compute the energy.

FIGURE 4
TYPICAL CALIBRATION PLOT OF TEMPERATURE RISE AS A FUNCTION OF THE CHARGING VOLTAGE SQUARED



The method requires no estimate of specimen resistance nor is it required that the specimen resistance remain constant during the discharge. No estimate of the absolute values of the constants of Equations 1 or 7 are required. Slight changes in the slope of the plot were found to occur from time to time. For most runs, therefore, a calibration plot was prepared before and after each run.

### b. Energy-measurement Method II

The second method employs the shunting resistor $R_2$ and an additional thermocouple element Tc 2, shown by dotted lines in Figure 1. The specimen resistance and the shunting resistor are arranged physically so that the inductive reactance at the oscillation frequencies employed are negligible in comparison with the corresponding resistances. The physical arrangement of the reaction cell and the shunting path will be described in a later section.

In effect, one thermocouple element is connected in series with the discharge current and is analogous to an ammeter. The second element is connected across the specimen wire and is analogous to a voltmeter. An analysis of the circuit is given in Appendix C, where it is shown that the specimen energy $E_1$ is given as follows:

$$E_1 = R_2 \sqrt{k_1 k_2} \sqrt{\Delta T_1 \Delta T_2} \left(1 - \frac{k_2}{k_1} \frac{\Delta T_2}{\Delta T_1}\right) , \qquad (8)$$

where $R_2$ is the resistance of the shunting path, $k_1$ and $k_2$ are calibration factors of each thermocouple element and are identical with the k of Equation 3, and $\Delta T_1$ and $\Delta T_2$ are the observed temperature rises of each thermocouple. Equation 8 depends only on the stability of the resistance $R_2$ and the thermocouple calibration factors $k_1$ and $k_2$. Changes in the charging voltage, extraneous circuit resistance, or specimen resistance have no effect on the energy calculation. The calibration constants are also independent of the frequency of the oscillations so long as the diameter of the constantan wires is sufficiently small so that the ac skin effect is negligible. The diameter of the constantan wire would have to exceed 140 mils for a 1% skin effect. The largest element used in the present study was 129 mils in diameter. The calibration constants were, therefore, independent of the number of condensers used in a discharge.

Determination of the calibration constants $k_1$ and $k_2$ was accomplished by making a series of short-circuited discharges, open-circuit discharges, and simulated runs using 64-mil nichrome wire specimens. The details of the calibration procedure are described in Appendix C. Experience has shown that only infrequent calibrations are required. The calibration constants were shown to be independent of the oscillation frequency by experiments described in Appendix C.

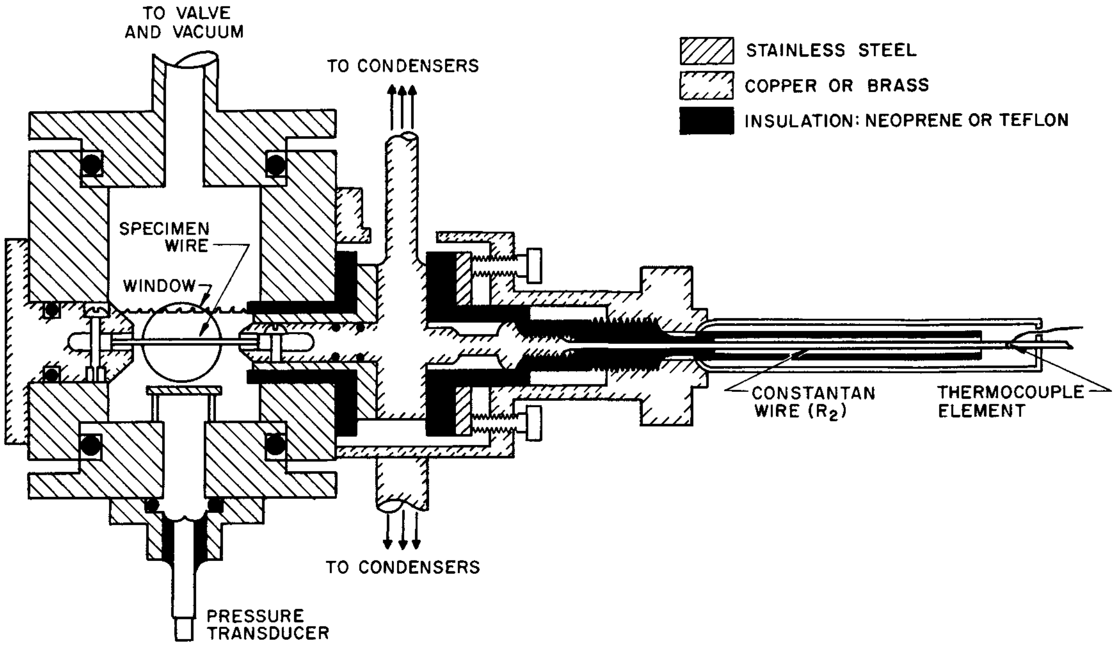
## B. Design of Reaction Cells

There are several unusual requirements on the design of a reaction cell for metal-water reaction studies by the condenser-discharge method. The cell must be vacuum and pressure tight. A cell designed for studies with heated water must also be leak-tight during thermal cycling. In addition, insulated leads of high current-carrying capacity must be brought into the cell.

## 1. Reaction Cell for Studies at Low Pressures

The reaction cell and the physical layout of the shunt path are shown in a schematic drawing in Figure 5 and in a photograph in Figure 6b. The cell was of stainless steel and had a volume of 75 cc. Specimen wires were mounted between massive copper rods. Specimen wires, one inch long and 30 or 60 mils in diameter, could be mounted. Electrical contact of the wire with the copper rods was achieved by means of split copper rings, $\frac{1}{8}$ in. in outer diameter and $\frac{3}{16}$ in. long, having an inner diameter equal to the diameter of the specimen wires. The copper rings were compressed between holes in the rods and the specimen wire by stainless steel screws embedded within the large rods. The use of new split rings for each discharge resulted in contacts of negligible resistance.

FIGURE 5
REACTION CELL FOR STUDIES AT LOW PRESSURES



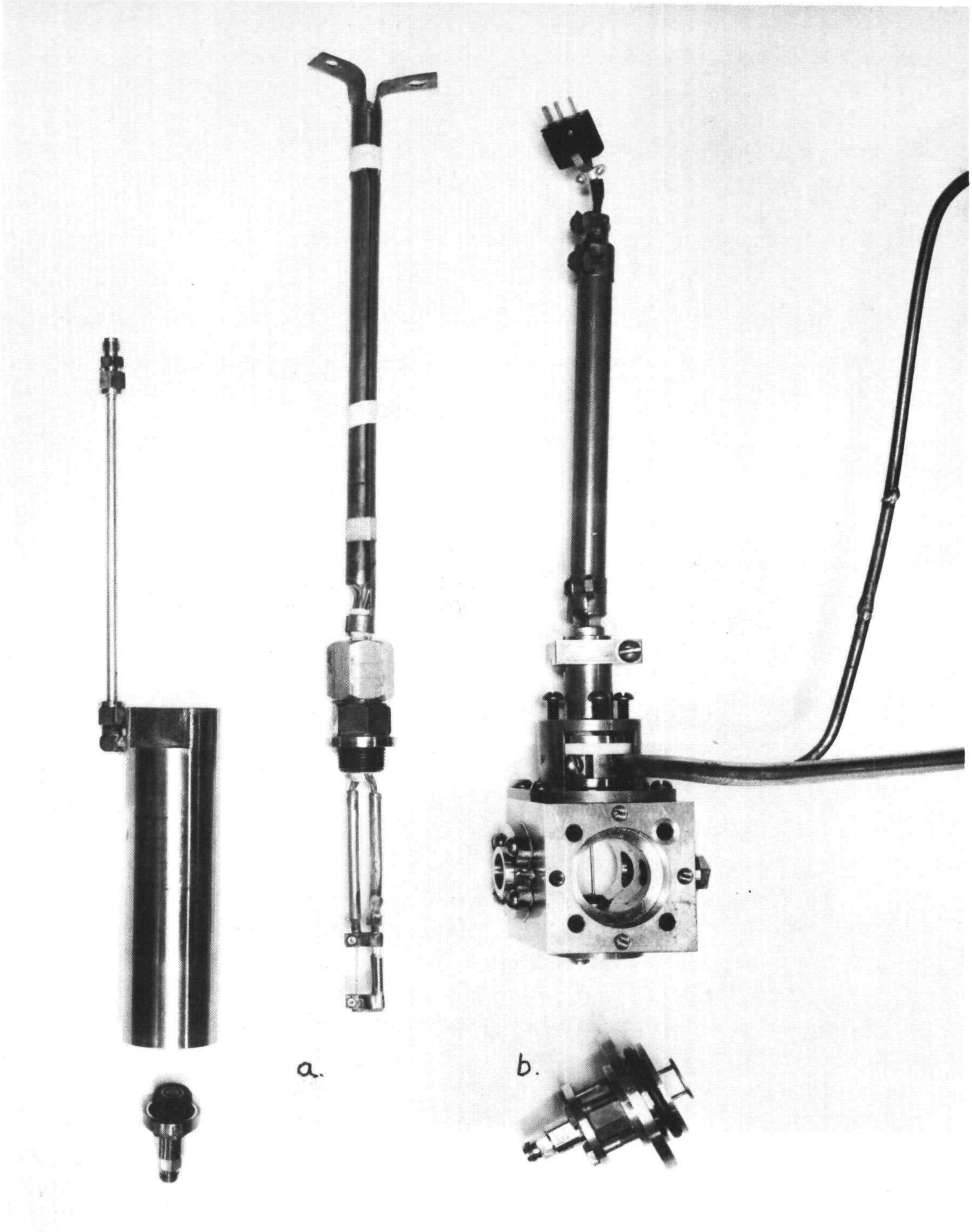
The discharge current was brought to the reaction cell by $\frac{1}{4}$-in. copper rods. Current was brought to the insulated side of the specimen wire as shown in Figure 5 and returned through the frame of the reaction cell. Current also flowed axially down a constantan resistance wire ($R_2$) and was returned along copper tubing which enclosed the resistance wire. Insulation was accomplished by means of machined Teflon inserts. Runs made using energy-measurement Method I were made with the resistance wire removed.

Vacuum and pressure sealing were accomplished by means of neoprene "O" rings which were lightly coated with high-vacuum stopcock grease.

Figure 6

PHOTOGRAPH OF REACTION CELLS

a. High Pressure Cell Components
b. Cell Assembly for Studies at Low Pressures



This allowed rapid assembly and disassembly with little likelihood of leakage. Parts were fastened together with steel cap screws, although they are not shown in Figure 5.

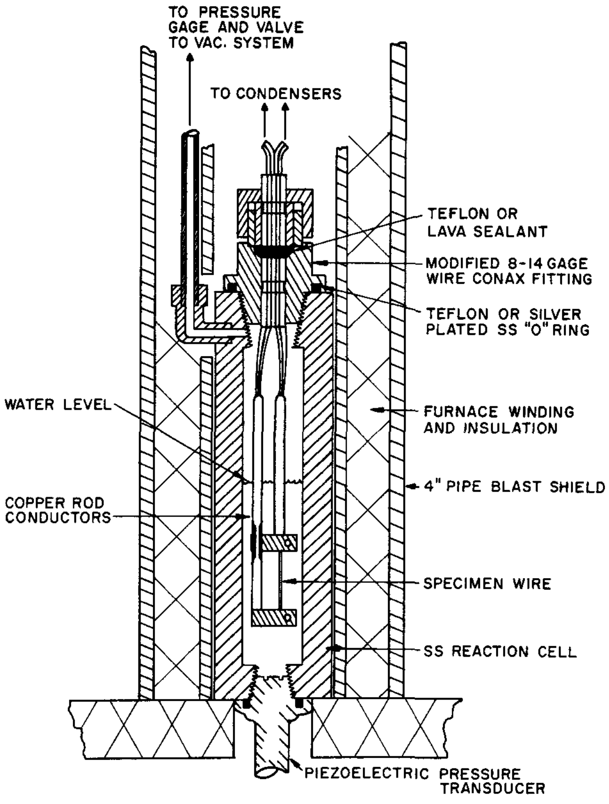
An SLM quartz crystal pressure transducer could be mounted in one of two places on the reaction cell. One, shown in Figure 5, was beneath the surface of the water and was mounted in a hard resin compound within a stainless steel flange to provide an insulated mounting. Direct impingement of the molten metal particles on the sensitive diaphragm of the transducer was prevented by a thin baffle. A transducer could also be mounted directly on the cell above the water level.

Direct or shadow motion pictures of the wire disintegration could be taken by means of two Pyrex windows mounted on the cell. The windows, one-half inch thick and one inch in diameter, were sealed in place using greased "O" rings.

### 2. Reaction Cell for Studies at High Pressures

The high-pressure cell is shown in Figure 6a and in Figure 7. It is constructed of stainless steel and has an internal diameter of one inch. Copper wire and rods were used as conductors within the cell. Specimens were mounted in copper-lined steel clamps. The discharge current was carried into the cell through eight 14-gauge wires by means of a large Conax Corp. fitting with a Teflon or a Lava sealant. An additional machined ring was silver-soldered to the standard fitting to hold a Teflon or a silver-plated stainless steel "O" ring to effect a positive seal that would withstand thermal cycling. An SLM pressure transducer was mounted in a similar fashion at the lower end of the cell.

FIGURE 7
REACTION CELL FOR STUDIES AT HIGH PRESSURES



The reaction cell after assembly and leak-testing was lowered into a heater constructed of two sizes of stainless steel pipe, as shown in Figure 7. The annulus between the two pipes contained nichrome heater windings, asbestos insulation, and control thermocouples. Both pipes act as blast shields in the event of an accident and would direct any projectiles either up or down.

## C. Auxiliary Instrumentation

### 1. High-speed Motion Pictures

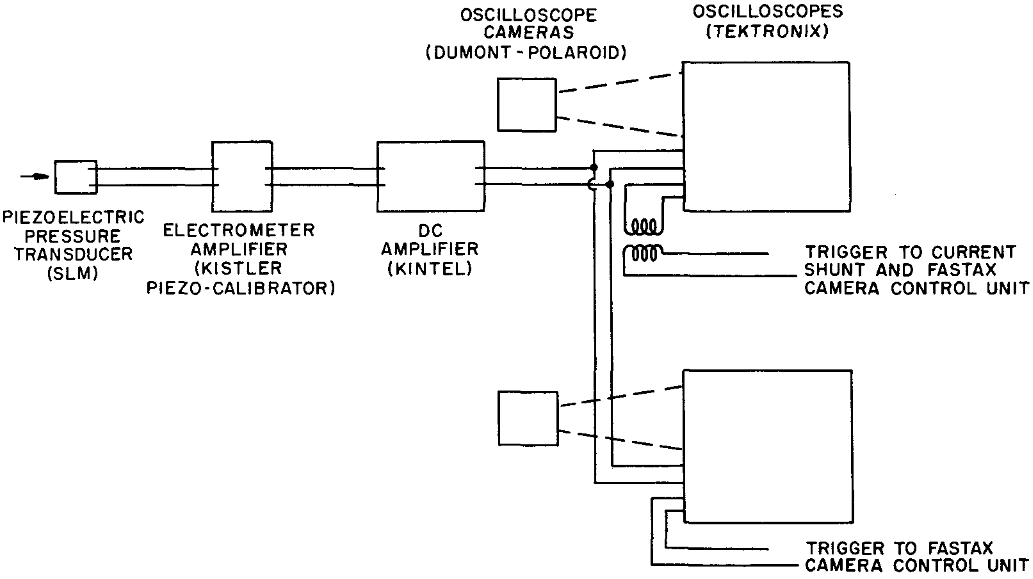
High-speed motion pictures were taken with a WF-17, 16-mm Fastax camera. The camera was operated with a commercial control unit utilizing time-delay relays. The camera was started manually. During typical operation, the film speed built up to approximately 3700 frames/sec after 0.6 sec when the discharge was initiated automatically. About one-third of the 100-ft roll is consumed during this period. Film speed reaches approximately 4700 frames/sec at the end of the roll. About 0.6 sec of reaction time is, therefore, photographed under these conditions. The camera was operated with a 2-in. lens, located 8 in. from the specimen, with a f/8 opening using TRI-X Reversal film. A Wratten red filter A (No. 25) was used to narrow the band pass of light produced by hot metal particles and thereby relate the intensity of the image more directly to the metal temperature.(36)

### 2. Measurement of Transient Pressure

The SLM piezoelectric transducers were chosen for the present application for their high sensitivity and rapid response. A pressure change of only 5 mm of mercury can be readily detected by means of suitable amplifying devices. Sensitivity to a differential change is, moreover, independent of the ambient pressure. A block diagram of the components used in conjunction with a transducer is shown in Figure 8. The frequency response of the transducer-electrometer combination is estimated by the manufacturer to be 4000 cycles/sec. The amplified signal was fed to the vertical plates of two cathode-ray oscilloscopes. One was used with a series of fast sweeps (normally 100-msec total sweep time).

FIGURE 8

CIRCUITRY USED FOR TRANSIENT PRESSURE MEASUREMENTS



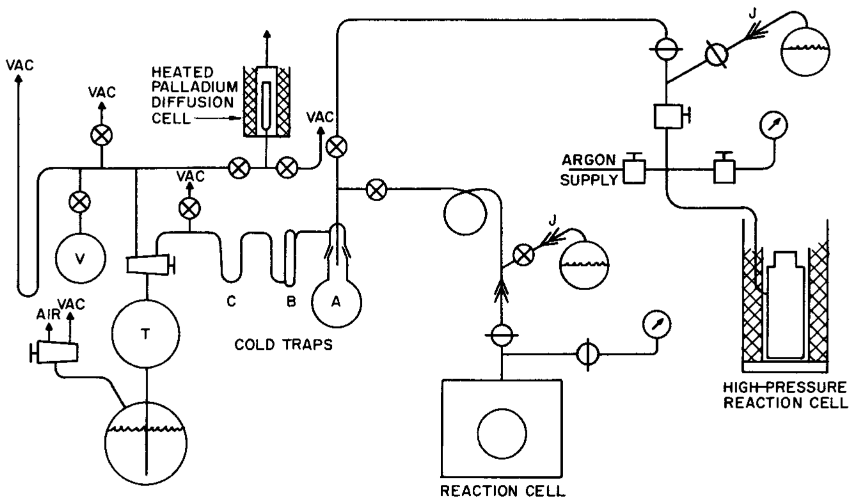
One sweep was fired simultaneously with the Fastax camera and gave a zero reference trace. A second sweep was triggered by the signal from the current shunt through an air-core transformer and, therefore, began simultaneously with the discharge current. A final sweep was fired as the control unit for the Fastax camera reset itself approximately 4 sec after the discharge, providing an indication of the "final" pressure. The second oscilloscope used a slow sweep covering a period of 2 sec and was fired simultaneously with the Fastax camera (0.6 sec before the discharge). In some cases, a final sweep was used to indicate the pressure after 10 sec. The slow sweep was momentarily blanked at one-second intervals by a circuit consisting of a synchronous motor and moving contacts. This provided accurate timing marks.

### 3. Gas-handling Apparatus

The reaction cells were connected with a Pyrex high vacuum apparatus as shown in a schematic diagram in Figure 9. The vacuum-producing apparatus consisted of a glass, two-stage mercury diffusion pump backed by a mechanical pump. Liquid nitrogen traps were used to retain the mercury vapor and prevent water from entering the pumps.

FIGURE 9

GAS-HANDLING APPARATUS ASSOCIATED WITH REACTION CELLS



## D. Run Procedure

The cell to be used was first assembled and then evacuated to 0.3 micron pressure or less. The water to be used in the run (35 to 50 cc) was first loaded into bulbs, indicated in Figure 9. The sequence: freezing, evacuating, and thawing, served to remove dissolved gases from the water. Water was then poured into the appropriate reaction cell by rotating the ground glass joint J (see Figure 9). The cells could then be isolated from the glass system by closing a metal valve and were then ready for a run.

### 1. Measurement of Total Extent of Reaction

Following a run in either cell, the gases in the reaction cell were expanded into a series of cold traps, indicated in Figure 9 as A, B, and C. The large trap A retained most of the water from the reaction cell without becoming plugged with ice. Traps B and C ensured complete water removal. Noncondensable gas was taken into Toepler bulb T and transferred over mercury into a collection manifold, indicated in Figure 9. Nine to fifteen cycles of the Toepler Pump resulted in complete transfer of noncondensable gases from the reaction cell and trap system into the collection manifold. Transfer was aided by the continual flow of water vapor from the cell to the cold trap A.

The total quantity of noncondensable gas in the collection manifold was determined by noting the pressure on the mercury manometer and the volume of the collection manifold (ca. 45 cc). Runs producing large quantities of hydrogen or runs with added argon gas required additional manifold volume V. The gas collected in the manifold was then opened to a heated palladium diffusion cell. All of the hydrogen contained in the collected gas diffused through the palladium in about one hour. All other gases remained in the manifold. From the pressure decrease and the total quantity of gas, the total hydrogen generated by reaction could be determined. Hydrogen purity generally exceeded 99 percent when no inert gas was deliberately added. Occasional mass spectrometric analyses* served to verify the results of the analytical procedure.

The total extent of reaction was then calculated from the hydrogen determination by means of the stoichiometric equation for the metal-water reaction and the gas laws.

### 2. Measurement of Particle Size of Residue

A method for estimating the total surface area and particle size of residue from runs was developed. For this a slide projector was specially constructed. Preliminary attempts using photomicrographs showed that a great number of separate photographs and an intricate sampling procedure were required. A magnification suitable for large particles would not allow diameter measurements of the smaller particles. It was necessary to have a very large blowup of the sample residue which could best be done by projection over a long optical arm, followed by tracing the image on large pieces of paper.

Particles were collected on filter paper following a run. After air drying, a representative quantity was obtained by successive division of the sample. The sample was then mounted on microscope slides by

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*Performed by the Chemistry Division, Argonne National Laboratory means of glyptal varnish. In many cases the entire sample could be mounted. Slides were projected and tracings prepared. Representative diameters of over 100 particles were then measured from the tracing. Sauter mean diameters were used to obtain a particle diameter representative of the entire residue of a run. The Sauter mean diameter for spherical particles is the diameter of spheres that would have the same surface-to-volume ratio as the entire sample:

$$D_{\text{Mean}} = \frac{\Sigma D^3}{\Sigma D^2} = 6\left(\frac{\text{Total Sample Volume}}{\text{Total Sample Surface}}\right)$$

## V. NATURE OF THE WIRE DISINTEGRATION

Runs were made with nominal 30- and 60-mil zirconium wires, drawn from arc-melted grade I crystal bar zirconium.* Chemical analysis** showed that metal had 19 parts per million carbon, 0.6 parts per million hydrogen, 11 parts per million nitrogen, and 77 parts per million oxygen. The results of a spectrographic analysis of the wires after drawing are shown in Table 1.

Table 1

ANALYSIS OF ZIRCONIUM WIRES
(Arc-melted Grade I crystal bar zirconium[a])
(Spectrographic analysis)

| Element[b] | ppm | Element[b] | ppm |
|---|---|---|---|
| B | 0.7 | Na | 14 |
| Cr | 3 | Ni | 30 |
| Cu | 30 | Pb | 14 |
| Fe | 300 | Si | 110 |
| Mn | 3 | | |

[a] Drawn into wires by Metallurgy Division, ANL.

[b] The analyses for those constituents not indicated were below the limits of spectrographic detection. Limits of detection are (in ppm): Ag 1, Al 10, As 10, Ba 20, Be 1, Bi 1, Ca 100, Co 1, K 20, Li 1, Hf 1000, Cd 100, Mg 1, Nb 20, P 50, Sb 1, Sn 5, Sr 100, Ti 20, V 10, Zn 20, W 100, Ta 1000.

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*Wires prepared by the Metallurgy Division, Argonne National Laboratory.

**Analyses by the Chemistry Division, Argonne National Laboratory.

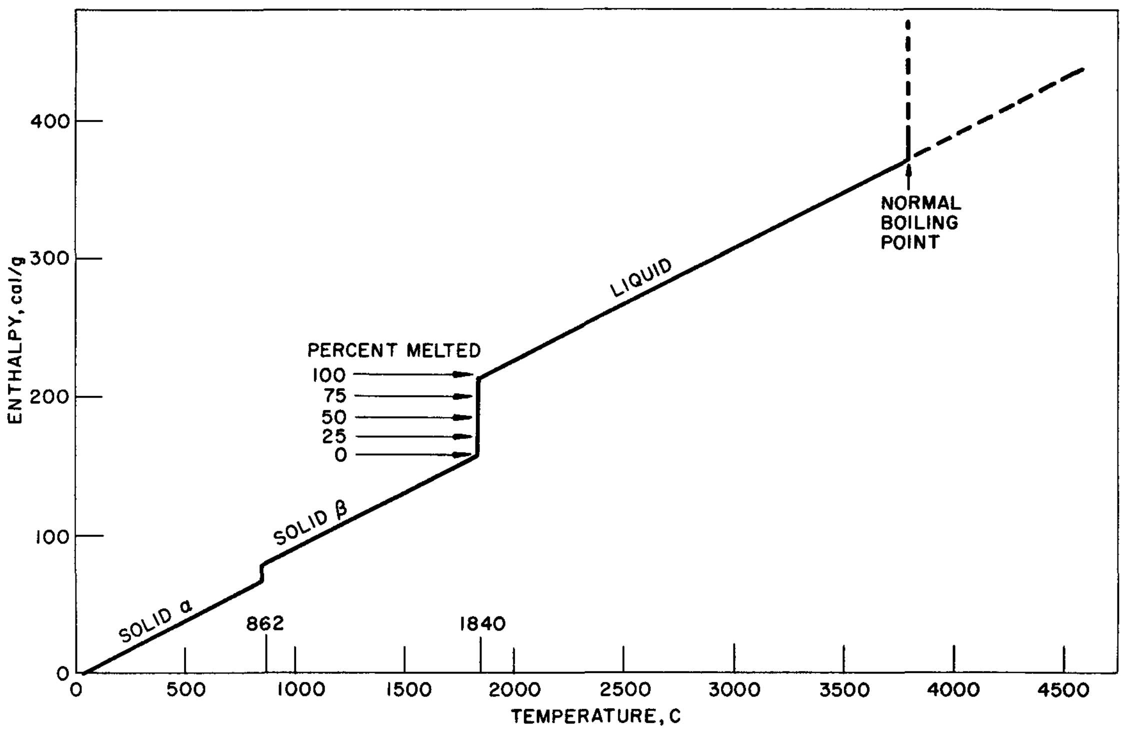
Runs were also made with 30-mil platinum wires. Such runs served to verify the energy-measurement method and to provide control experiments with a metal that would not react with water. Platinum had the advantage that its melting point (1773 C) was similar to that of zirconium (1840 C).

## A. Correlation of Energy Input with the Appearance of the Residue

Data from runs in the low-pressure cell are presented in Table 2. The calculated energy inputs to zirconium and platinum wire specimens are given. The temperatures reached by the wires were calculated from enthalpy data on the assumption that adiabatic heating occurred. Enthalpy data for zirconium(37) are plotted in Figure 10. Residues from typical zirconium runs were mounted on microscope slides. Pictures of these residues are shown in Figure 11. Clear material in the figure is the glyptal varnish used to mount the residue.

FIGURE 10

ENTHALPY-TEMPERATURE DATA FOR ZIRCONIUM(37)



It is evident from the results that a very reasonable correlation exists between the calculated initial metal temperature and the appearance of the residue. Specimens calculated to have an initial temperature up to the melting point remained intact, as shown in Figure 11a. Energy values corresponding to between 0 and 50 percent melted left zirconium wires essentially intact but distorted into an elliptical shape, as shown in Figure 11b.

Table 2

RESULTS OF RUNS IN THE LOW PRESSURE CELL

| Run | Energy Input (cal/g) | Calc Metal Temp (C) *and Physical State* | % Reaction | Metal Particle Diameter ($\mu$) | Appearance of Residue |
|---|---|---|---|---|---|
| Runs with 60-mil Zirconium Wires | | | | | |
| 32 | 100 | 1100, solid | 0.7 | 2140 | Intact |
| 23 | 127 | 1500, solid | 1.2 | 2180 | Intact |
| 13 | 137 | 1600, solid | 3.9 | 2160 | Intact |
| 22 | 150 | 1800, solid | 4.2 | 2170 | Intact |
| 24 | 158 | 1840, 10% liquid | 5.9 | 2060 | Elliptical |
| 28 | 174 | 1840, 30% liquid | - | 2180 | Elliptical |
| 27 | 183 | 1840, 50% liquid | - | 2240 | Elliptical |
| 25 | 190 | 1840, 60% liquid | 8.9 | 2280 | Spherical |
| 52 | 198 | 1840, 70% liquid | 10.2 | 1740 | Spherical Particles |
| 26 | 203 | 1840, 80% liquid | 7.9 | 2100 | Spherical Particles |
| 29 | 209 | 1840, 90% liquid | 7.9 | 1500 | Spherical Particles |
| 14 | 217 | 1900, liquid | 8.2 | 1960 | Elliptical |
| 15 | 218 | 1900, liquid | 9.0 | 2040 | Spherical Particles |
| 18 | 233 | 2100, liquid | 12.1 | 1500 | Spherical Particles |
| 30 | 235 | 2100 liquid | 12.6 | 940 | Spherical Particles |
| 31 | 258 | 2400, liquid | 18.3 | 680 | Spherical Particles |
| 42 | 269 | 2500, liquid | 10.9 | 740 | Spherical Particles |
| 20 | 275 | 2600, liquid[a] | 24.0 | 440 | Spherical Particles |
| 19 | 276 | 2600, liquid[a] | 43.0 | 340 | Spherical Particles |
| 16 | 284 | 2700, liquid | 17.1 | 980 | Spherical Particles |
| 40 | 290 | 2800, liquid[a] | 39.0 | 160 | Spherical Particles |
| 41 | 294 | 2800, liquid[a] | 71.0 | 110 | Spherical Particles |
| 17 | 296 | 2900, liquid[a] | 45.0 | 340 | Spherical Particles |
| 39 | 300 | 2900, liquid[a] | 50.0 | 240 | Spherical Particles |
| 21 | 313 | 3100, liquid[a] | 37.0 | 240 | Spherical Particles |
| 53 | 322 | 3200 liquid[a] | 51.0 | 370 | Spherical Particles |
| 37 | 332 | 3300, liquid[a] | 52.0 | 180 | Spherical Particles |
| 35 | 361 | 3700, liquid[a] | 60.0 | 200 | Spherical Particles |
| 34 | 388 | 4100, liquid[a] | 71.0 | 270 | Spherical Particles |
| 36 | 393 | 4100, liquid[a] | 50.0 | 480 | Spherical Particles |
| Runs with 30-mil Zirconium Wires | | | | | |
| 85 | 124 | 1500, solid | 5.9 | 1120 | Intact |
| 86 | 146 | 1700, solid | 10.0 | 1130 | Two Pieces |
| 71 | 149 | 1800, solid | 8.6 | 1160 | Four Pieces |
| 88 | 160 | 1840, 10% liquid | 13.7 | 1100 | Elliptical |
| 89 | 163 | 1840, 10% liquid | 12.3 | 1010 | Elliptical |
| 87 | 165 | 1840, 20% liquid | 15.6 | 1010 | Elliptical |
| 75 | 180 | 1840, 40% liquid | 12.6 | 1040 | Elliptical |
| 76 | 182 | 1840, 40% liquid | 16.4 | 1040 | Elliptical |
| 72 | 190 | 1840, 60% liquid | 11.8 | 1630 | Spherical Particles |
| 107 | 198 | 1840, 70% liquid | 13.8 | 1390 | Spherical Particles |
| 82 | 214 | 1840, 100% liquid | 18.5 | 1200 | Spherical Particles |
| 90 | 214 | 1840, 100% liquid | 19.7 | 1290 | Spherical Particles |
| 108 | 231 | 2100, liquid | 14.8 | 1680 | Spherical Particles |
| 106 | 232 | 2100, liquid | 18.1 | 1020 | Spherical Particles |
| 83 | 241 | 2200, liquid | 14.8 | 1180 | Spherical Particles |
| 112 | 255 | 2400, liquid | 15.3 | 1610 | Spherical Particles |
| 74 | 270 | 2500, liquid | 23.9 | 780 | Spherical Particles |
| 109 | 290 | 2800, liquid[a] | 43.8 | 300 | Spherical Particles |
| 111 | 296 | 2900, liquid[a] | 22.6 | 650 | Spherical Particles |
| 110 | 314 | 3100, liquid[a] | 45.7 | 320 | Spherical Particles |
| 73 | 324 | 3200, liquid[a] | 44.9 | 330 | Spherical Particles |
| 113 | 387 | 4000, liquid[a] | 38.0 | 420 | Spherical Particles |
| 114 | 482 | - , part vapor[a] | 49.7 | 440 | Spherical Particles |
| Runs with 30-mil Platinum Wires | | | | | |
| 91 | 40 | 1150, solid | - | 1150 | Intact |
| 92 | 43 | 1200, solid | - | 1150 | Intact |
| 93 | 54 | 1500, solid | - | 1150 | Intact |
| 102 | 71 | 1773, 20% liquid | - | 1160 | Intact |
| 94 | 73 | 1773, 30% liquid | - | 1140 | Intact |
| 96 | 77 | 1773, 40% liquid | - | 1150 | Intact |
| 103 | 82 | 1773, 60% liquid | - | - | Intact (Bent) |
| 104 | 84 | 1773, 70% liquid | - | 1830 | Spherical Particles |
| 100 | 88 | 1773, 80% liquid | - | 1260 | Spherical Particles |
| 101 | 92 | 1773, 100% liquid | - | 1410 | Spherical Particles |
| 99 | 94 | 1800, liquid | - | 1470 | Spherical Particles |
| 97 | 114 | 2250, liquid | - | 1040 | Spherical Particles |
| 105 | 136 | 2600, liquid | - | 960 | Spherical Particles |

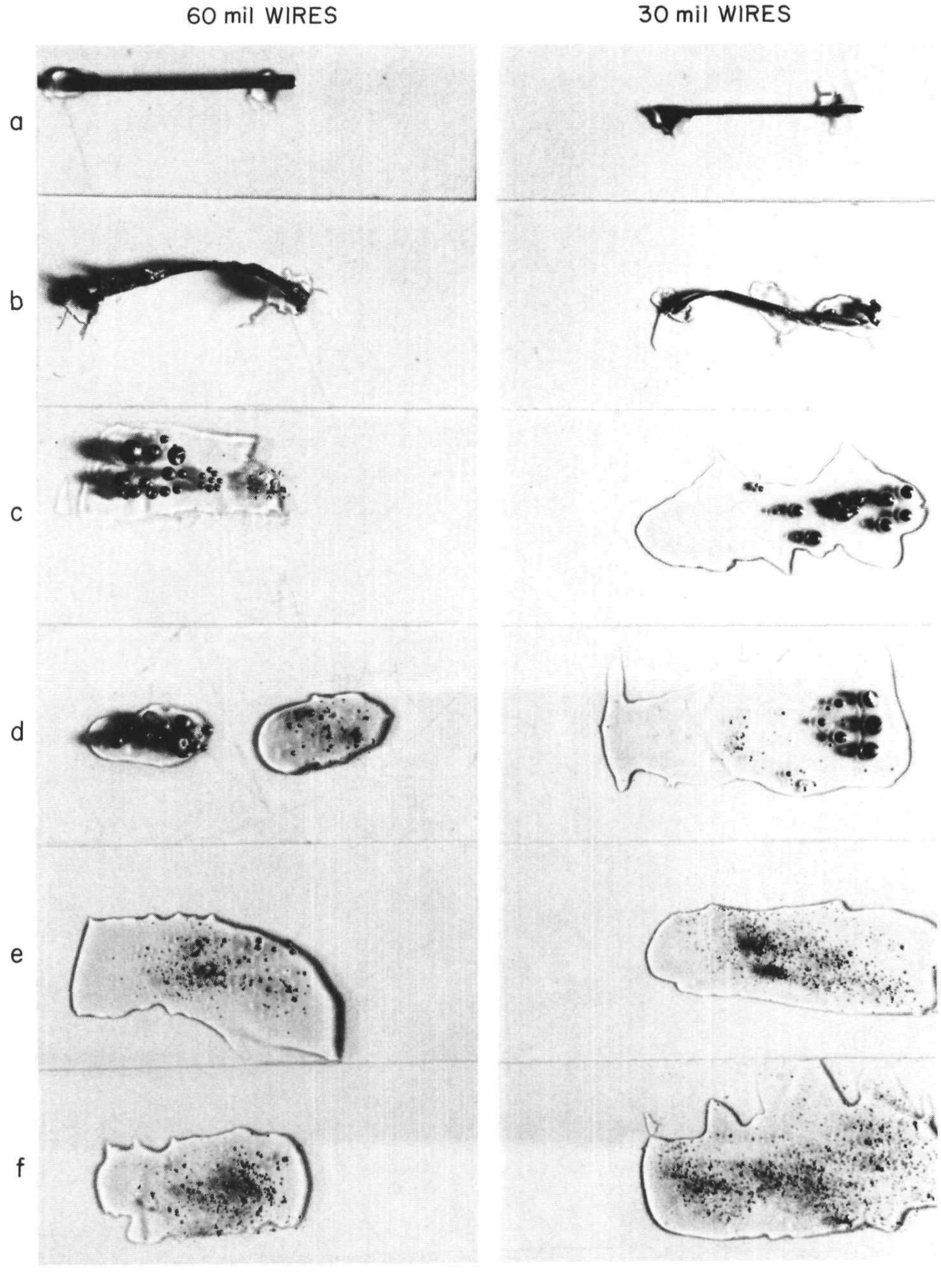
[a] Runs had an explosive pressure rise

Figure 11

PHOTOGRAPHS OF ZIRCONIUM RUN RESIDUES
(MOUNTED ON MICROSCOPE SLIDES)

Calculated Initial Temperature, C

a. 1500, Solid
b. 1840, 30-40% Liquid
c. 1840, 70-80% Liquid
d. 2400-2500, Liquid
e. 2800, Liquid
f. 3100-3300, Liquid

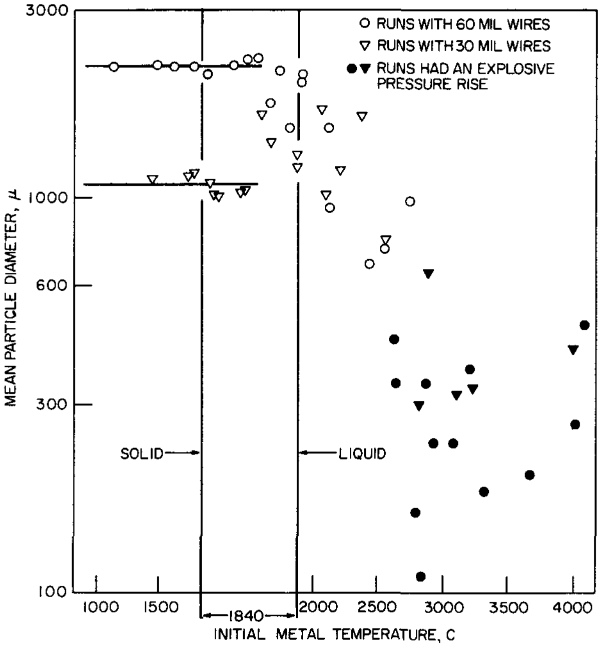


At greater energy values, spherical particles were formed with progressively smaller diameters. Residue from platinum runs did not pass through the elliptical shape, but went directly from the original cylindrical shape into spherical particles at energies corresponding to between 50 and 70 percent melted. The physical evidence of melting at energies corresponding to the melting point is the most significant check of the energy-measurement methods and the assumption of adiabatic heating.

## B. Particle Diameters

The results of particle size measurements for zirconium runs in room-temperature water are included in Table 2 and plotted in Figure 12. The particle diameters quoted for specimens that remained intact are those of spheres that would have the same surface-to-volume ratio as the wires. For 60-mil wires, this diameter is 90 mils, or 2280 $\mu$. Zirconium runs with initial metal temperatures of 2600 C or higher generally resulted in significantly smaller particles. With the exception of two runs, a calculated initial temperature of 2600 C or higher resulted in a mean particle diameter of 480 $\mu$ or less, whereas initial temperatures below 2600 C gave mean diameters above 680 $\mu$. This behavior is also evident in Figure 11.

FIGURE 12
MEAN PARTICLE DIAMETER OF RESIDUE FROM ZIRCONIUM RUNS IN ROOM-TEMPERATURE WATER AS A FUNCTION OF CALCULATED INITIAL METAL TEMPERATURE



Very uniform powders were produced in very energetic runs. It is likely that the oxide $ZrO_2$ which begins to form immediately stabilizes the larger particles of molten metal. $ZrO_2$, however, melts at 2700 C, so that particles having higher initial temperatures would not be stabilized in an early stage of the wire disintegration. Further subdivision could then occur.

The Sauter mean diameter used to correlate the results is more greatly influenced by large particles than by small particles. One large particle in residue from a run can lead to a significant increase in the mean diameter.

It is apparent from results shown in Figure 12 that particles from runs with 30-mil wires were sometimes larger than the original wire. This was probably due to surface forces drawing a considerable length of wire together to form a single particle.

### C. High-speed Motion Pictures

Typical film sequences from zirconium runs are shown in Figure 13. The film speed was approximately 4000 frames/sec, so that heating (in 0.3 msec) occurred in one or two frames. The first frame in each sequence indicates that uniform heating did occur along the length of the wire. Control films of a tungsten ribbon lamp taken under identical conditions showed that an image is barely detectable at temperatures near 1300 C. Both the optical pyrometer used to determine tungsten temperature and the film (with the red filter) respond to light in a region of wave length near 0.65 $\mu$. Image intensities of specimens shown in Figure 13 and those of other runs were not inconsistent with the calculated initial temperatures.

Rapid generation of steam and hydrogen interferes with the image, since the wires are under water. The disintegration of the wire into particles is, therefore, not clearly visible. A brief series of runs was made in an argon environment. Typical runs are shown in Figure 14. Four milliseconds of time are visible in the sequences.. It is apparent that although heating occurred in a fraction of a millisecond, several milliseconds were required for the molten wire to form particles at temperatures slightly above the melting point, whereas in runs at very high temperature the wire disintegrated very rapidly.

The sequence shown in Figure 14c illustrated a very interesting phenomenon described in Reference 38. The molten filament of metal bulges at regular intervals along its length. The regular undulating pattern described by the metal is shown to be due to mechanical forces of expansion and surface forces. The tendency of 60-mil wires to form about 10 large spherical particles is seen in the pictures of the residue shown in Figure 11c and 11d. Wires heated under water are influenced both by the stabilizing action of oxide formation and rapid quenching.

Discharge conducted in a vacuum environment (0.1 to 1 $\mu$ pressure) were accompanied by a powerful arc which bypassed the wire. Energy calculations were, therefore, not consistent with the occurrence of melting.

Figure 13

HIGH SPEED MOTION PICTURES OF RUNS WITH 30-MIL ZIRCONIUM WIRES IN WATER

(4000 frames/sec)

Calculated Initial Temperature, C

a. 1840, 10% Liquid
b. 1840, 100% Liquid
c. 2400, Liquid
d. 3100, Liquid
e. (482 cal/g), Vapor

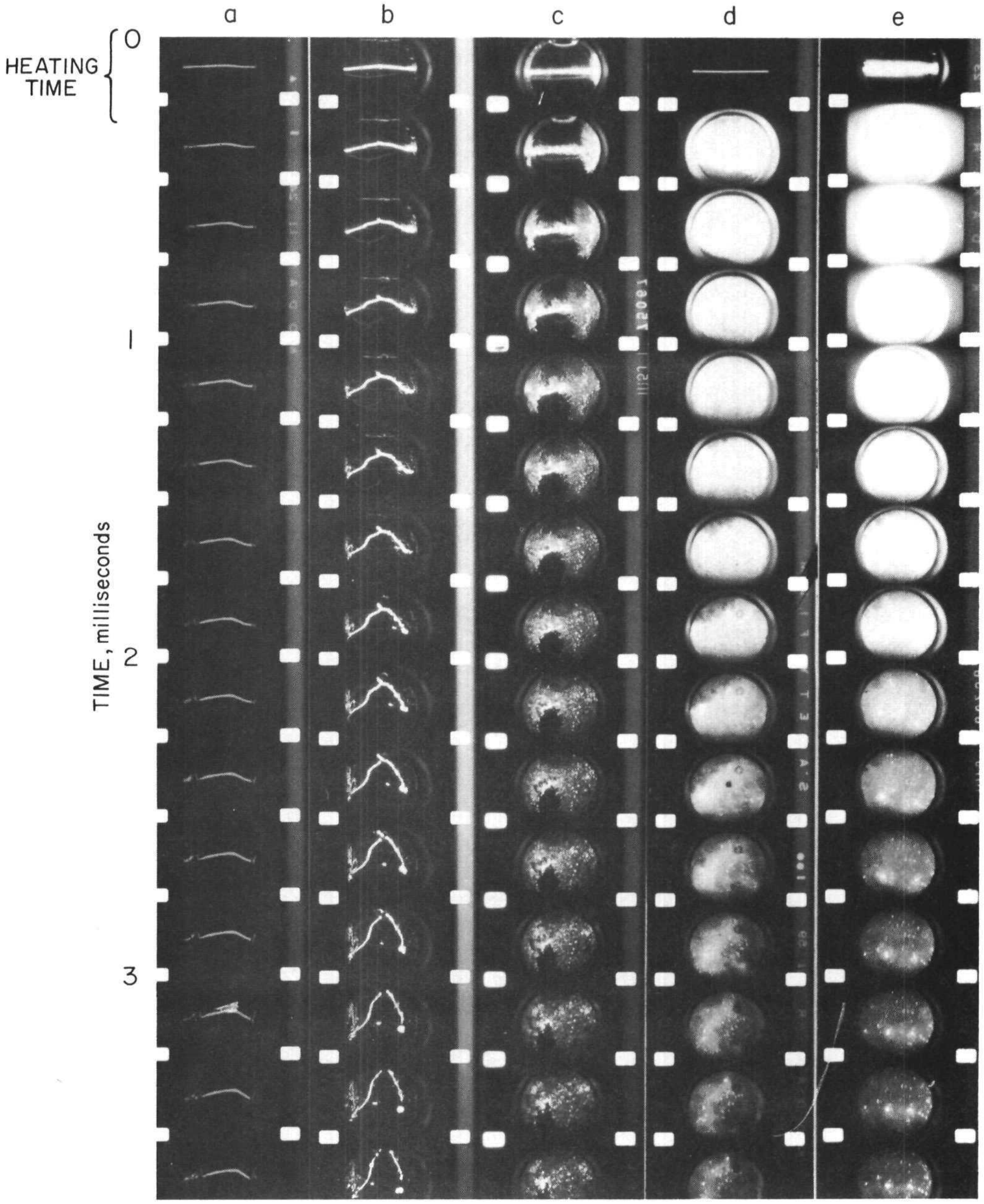


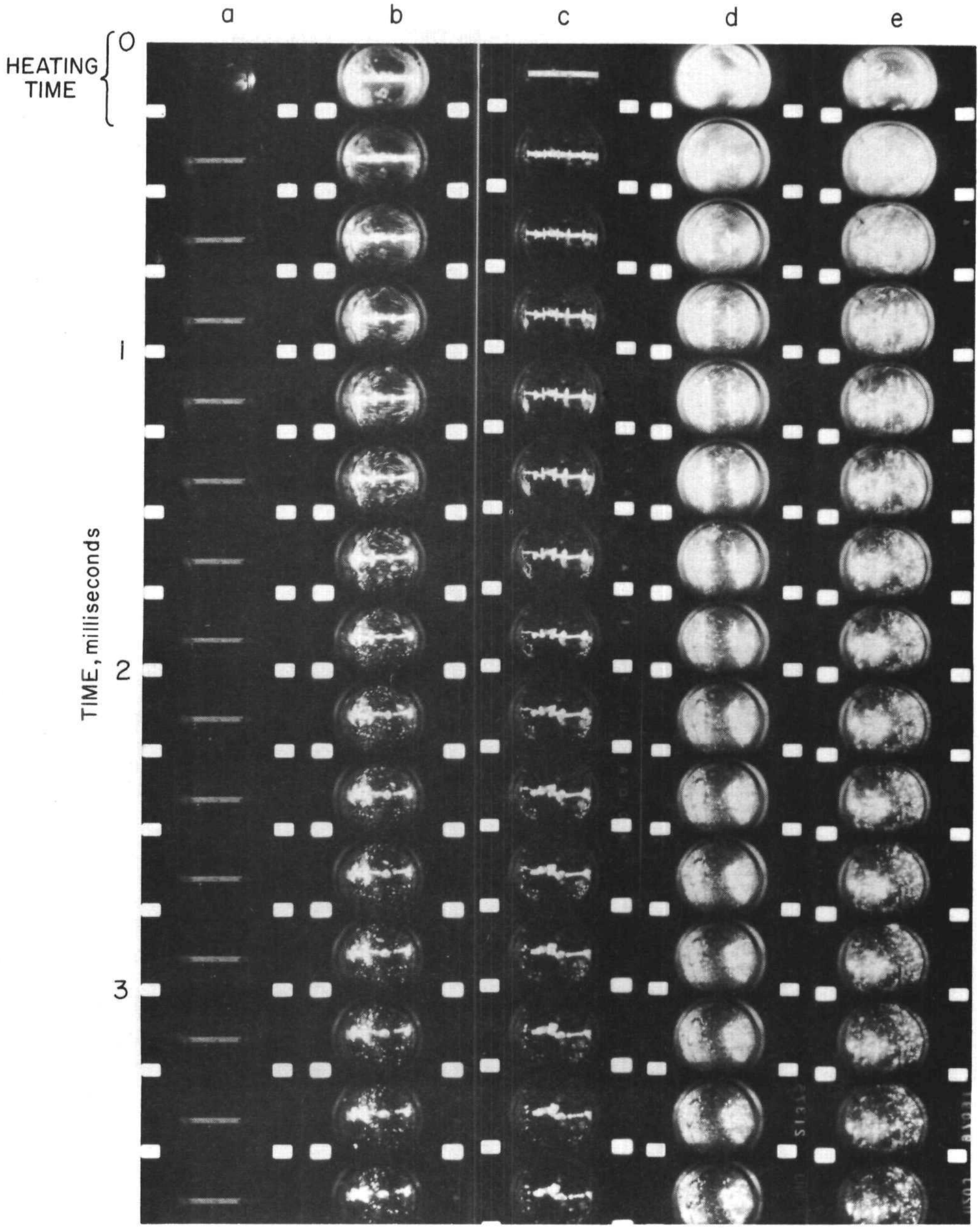
Figure 14

HIGH SPEED MOTION PICTURES OF RUNS WITH 60-MIL ZIRCONIUM WIRES IN ARGON ATMOSPHERE

(4000 frames/sec)

Calculated Initial Temperature, C

a. 1700, Solid
b. 1840, 70% Liquid
c. 1840, 80% Liquid
d. 2700, Liquid
e. 2900, Liquid



# VI. PRELIMINARY RESULTS WITH ZIRCONIUM

Complete results and a detailed analysis of the zirconium-water reaction will be published separately. The preparation of this manuscript is in an advanced stage.

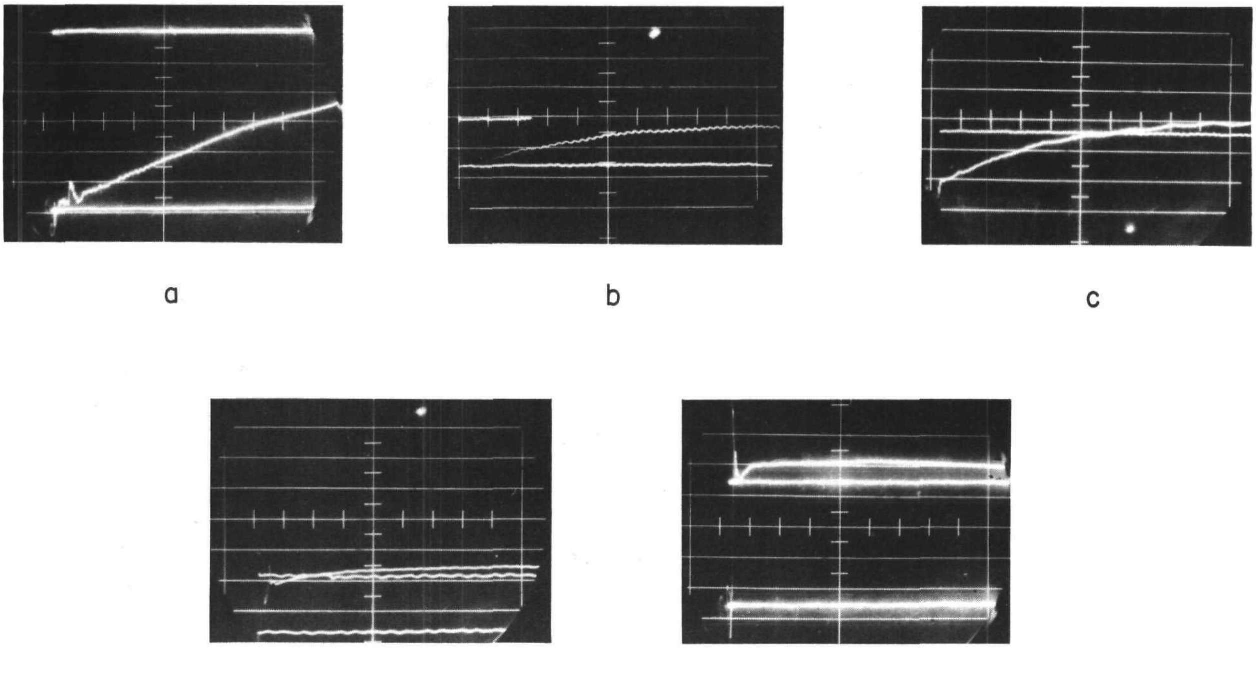
## A. Rate of Pressure Rise

Two series of pressure traces obtained with the piezoelectric pressure transducer are reproduced in Figures 15 and 17. Pressure-time curves deduced from the traces are presented in Figures 16 and 18. The runs to which Figures 15 and 16 correspond were made with 60-mil zirconium wires and the traces have the high-speed sweep.

Figure 15

PRESSURE TRACES FROM RUNS WITH 60-MIL ZIRCONIUM WIRES
(Sweeps fired: -0.5, 0.0, and 4.0 sec relative to discharge)

| | Run No. | Initial Metal Temp, C. and Physical State | Pressure Rise, atm | Sensitivity, atm/cm | Sweep Rate, msec/cm |
|---|---|---|---|---|---|
| (a) | 52 | 1840, 70% Liquid | 0.47 | 0.080 | 10 |
| (b) | 18 | 2100, Liquid | 0.56 | 0.36 | 10 |
| (c) | 16 | 2700, Liquid | 0.60 | 0.37 | 10 |
| (d) | 19 | 2600, Liquid | 1.90 | 1.04 | 5 |
| (e) | 53 | 3200, Liquid | 1.93 | 0.48 | 10 |

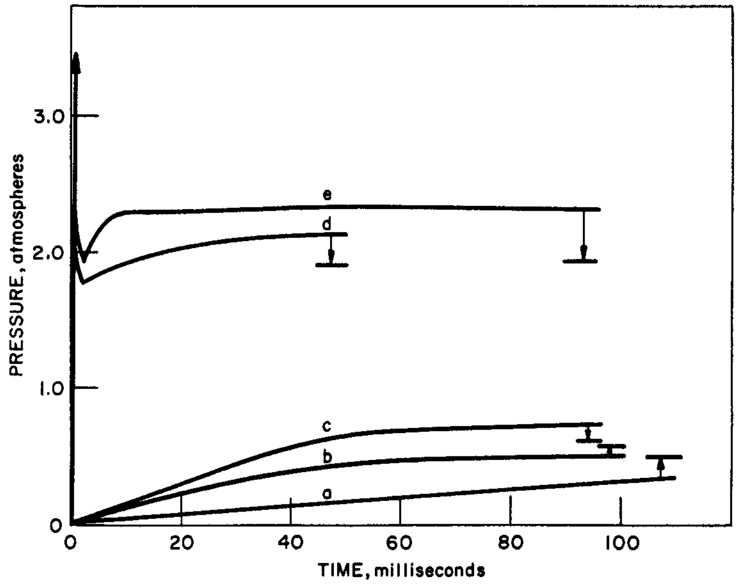


a b c

d e

Figure 16

PRESSURE-TIME CURVES TAKEN FROM THE OSCILLOGRAMS OF FIGURE 15
(60-mil Zirconium Wires)



The runs are clearly divisible into two categories. Runs with calculated initial metal temperatures up to ca. 2600 C had slow pressure rise rates, as shown in a, b, and c of Figures 15 and 16.* It required from one-tenth to several tenths of a second for the pressure to approach a final value. Runs with calculated initial metal temperatures exceeding 2600 C showed an explosive pressure rise, as shown in d and e of Figures 15 and 16. A final pressure was reached within a few milliseconds.

Some electrical noise inevitably occurred at the time of the discharge. It was generally impossible to establish the character of the pressure within the first millisecond. No estimate of the peak explosion pressure was, therefore, possible. Noise spikes occurred in a number of traces which were apparently not associated with an explosion. When a real explosion occurred, the trace returned rapidly to the final pressure. A noise spike, however, returned to a near initial pressure and then reproduced the slowly increasing pressure.

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* Run 16 shown in Figure 15c had a calculated initial metal temperature of 2700 C and was the only zirconium run in room-temperature water at metal temperature above 2600 C to show the slow pressure rise.

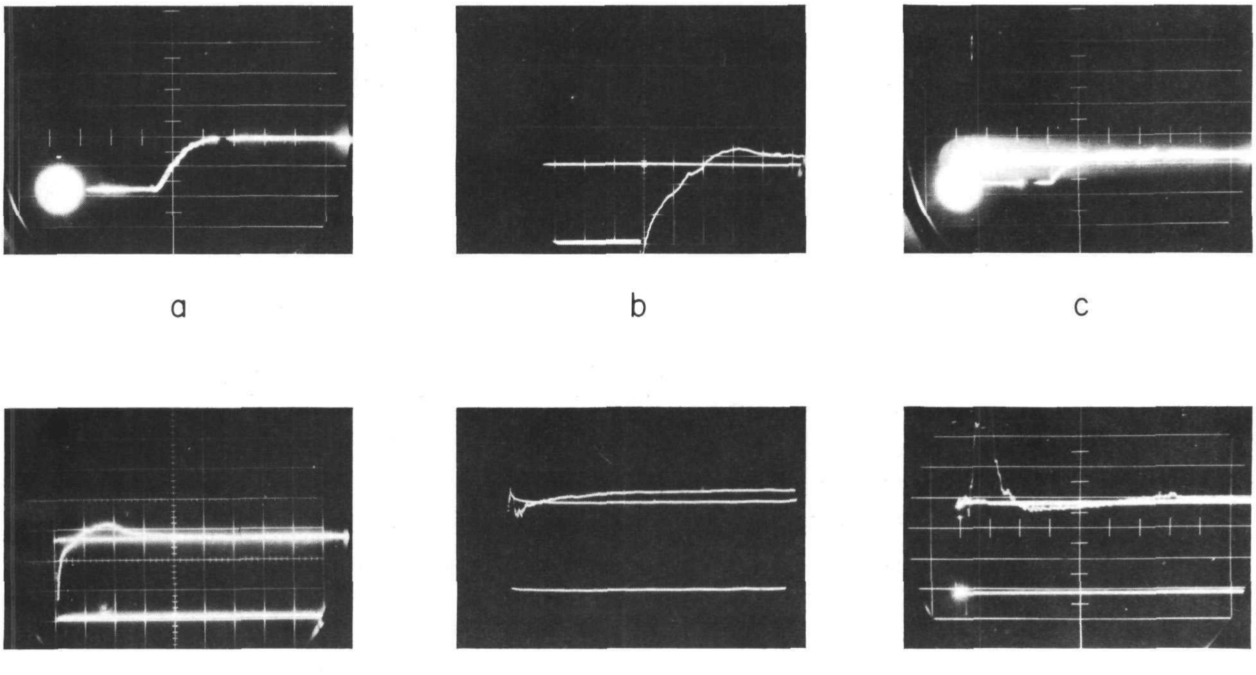
Traces reproduced in Figure 17 and plotted in Figure 18 were obtained with 30-mil wires. Four nonexplosive runs, shown in a, b, c, and d of Figures 17 and 18, were obtained using the slow sweep. The bright spot apparent in Figure 17a and 17c is an overexposed image of the beam registered between the time the camera was opened and the trace was fired. It was apparent that some over-pressure occurred because of the relatively rapid heating even in the nonexplosive runs. The extreme rapidity of explosive runs is apparent in Figures 17f and 18f for runs in which a very fast sweep was used.

Figure 17

PRESSURE TRACES FROM RUNS WITH 30-MIL ZIRCONIUM WIRES

(Sweep firing varied, normally -0.5, 0.0, and 4.0 sec relative to discharge)

| | Run No. | Initial Metal Temp, C. and Physical State | Pressure Rise, atm | Sensitivity, atm/cm | Sweep Rate, msec/cm |
|---|---|---|---|---|---|
| (a) | 86 | 1700, Solid | 0.11 | 0.063 | 220 |
| (b) | 82 | 1840, 100% Liquid | 0.16 | 0.063 | 200 |
| (c) | 106 | 2100, Liquid | 0.16 | 0.177 | 220 |
| (d) | 74 | 2500, Liquid | 0.22 | 0.088 | 200 |
| (e) | 109 | 2800, Liquid | 0.44 | 0.156 | 10 |
| (f) | 114 | (482 cal/g) Vapor | 0.46 | 0.156 | 1 |

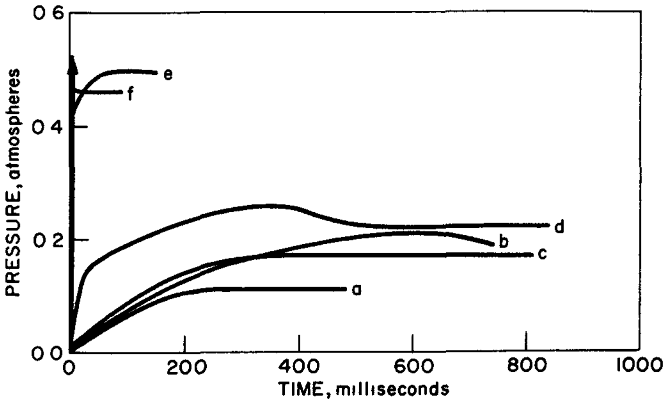


a b c

d e f

Figure 18

PRESSURE-TIME CURVES TAKEN FROM THE OSCILLOGRAMS OF FIGURE 17
(30-mil Zirconium Wires)



## B. Total Extent of Reaction

Results of the total extent of reaction as determined by hydrogen analyses are included in Table 2 for runs made in the low-pressure cell. Results for runs made in the high-pressure cell are given in Table 3.

Table 3

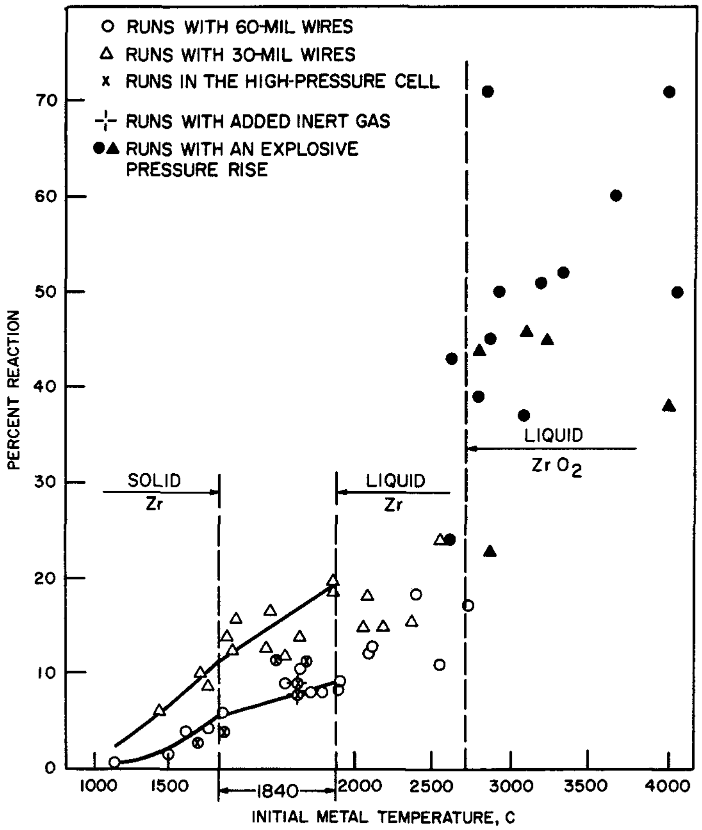
RESULTS OF 60-MIL ZIRCONIUM RUNS IN THE HIGH-PRESSURE CELL

| Run No | Energy Input (cal/g) | Calc Metal Temp (C) and Physical State | Saturated Vapor Pressure of Water (psia) | Pressure of Added Argon (psi) | % Reaction |
|---|---|---|---|---|---|
| Runs with Room Temperature Water | | | | | |
| 192 | 144 | 1700, solid | 0 5 | 0 | 2 6 |
| 193 | 157 | 1840 solid | 0 5 | 0 | 3 7 |
| 202 | 185 | 1840 50% liquid | 0 5 | 0 | 11 3 |
| 205 | 195 | 1840, 70% liquid | 0 5 | 20 | 7 7 |
| 204 | 195 | 1840 70% liquid | 0 5 | 25 | 8 9 |
| 197 | 201 | 1840, 80% liquid | 0 5 | 0 | 11 2 |
| Runs with Water at 90-125 C | | | | | |
| 194 | 150 | 1800 solid | 10 | 0 | 8 6 |
| 191 | 150 | 1800 solid | 32 | 0 | 7 8 |
| 196 | 204 | 1840, 80% liquid | 22 | 0 | 31 5 |
| 206 | 205 | 1840, 80% liquid | 26 | 23 | 37 6 |
| 200 | 216 | 1840 100% liquid | 19 | 0 | 51 7 |
| Runs with Water at 140-200 C | | | | | |
| 195 | 157 | 1840 solid | 215 | 0 | 9 0 |
| 190 | 161 | 1840 10% liquid | 225 | 0 | 8 5 |
| 189 | 169 | 1840 20% liquid | 205 | 0 | 14 5 |
| 203 | 203 | 1840 80% liquid | 50 | 0 | 55 2 |
| 188 | 206 | 1840 80% liquid | 155 | 0 | 30 7 |

Data for runs with water at room temperature (initial pressure ca. 0.5 psi) are plotted in Figure 19. Runs made in both reaction cells are included in the figure and indicate that there was no significant apparatus effect even though wires are mounted horizontally in the low-pressure cell and vertically in the high-pressure cell. Included in Figure 19 are two runs made with an over-pressure of argon gas. There is also no apparent effect of inert gas over-pressure. Approximately twice as much reaction occurs with the 30-mil wires as with the 60-mil wires up through the melting point region. The original wire size has a less important effect at higher initial metal temperatures. It was shown in Figure 12 that differences in particle diameters of residue from 30- and 60-mil wires largely disappeared above the melting point region.

Figure 19

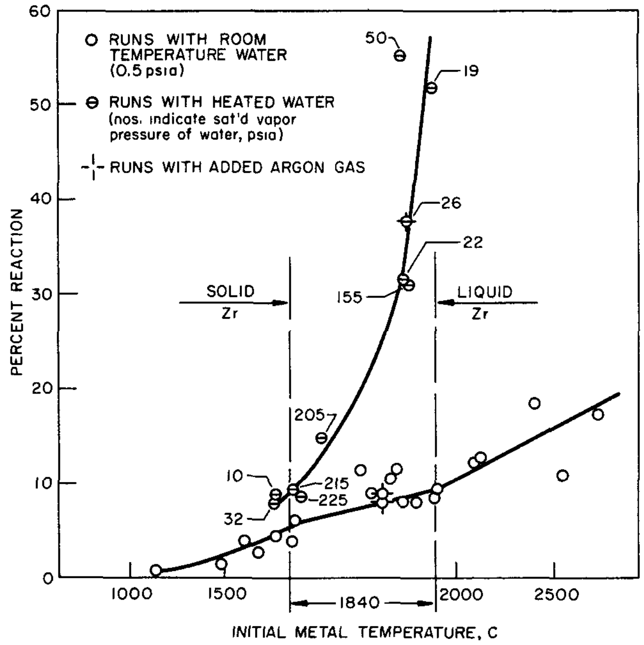
RESULTS OF ZIRCONIUM RUNS IN ROOM-TEMPERATURE WATER



A series of runs was made with 60-mil wires at elevated water temperature and a correspondingly higher pressure. The runs were made in the high-pressure reaction cell and the results are plotted on Figure 20 along with runs made with room-temperature water (vapor pressure ca. 0.5 psi). The number associated with each data point is the saturated vapor pressure of the water in psi used in the run. The results show that, although inert gas pressure had no apparent effect on the reaction, increased water vapor pressure had an important effect.

Figure 20

RESULTS OF RUNS WITH 60-MIL ZIRCONIUM WIRES



Runs in which the water vapor pressure ranged from 10 to 225 psi (water temperature from 90 to 200 C) gave a considerably greater extent of reaction than runs made with water at room temperature. There appeared to be no effect, however, of water vapor pressure (or water temperature) in the range between 10 and 225 psi. Additions of inert gas to runs in heated water again had no major effect. Pressure traces from runs reported in Table 3 showed only the slow rate of pressure rise.

## C. Analysis of Results

The nature of the results indicates that the rates of both a chemical reaction and a gaseous diffusion process must be considered. This follows from the observation that the extent of reaction does not increase regularly with increasing water vapor pressure (or water temperature). It appears likely that the differences between runs in room-temperature water and those in heated water are primarily a function of the degree of subcooling* of the water. Heat transfer and presumably also gaseous diffusion

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* A subcooled liquid is one that is at a temperature below its boiling point. Room-temperature water rapidly becomes subcooled as the pressure increases during a run because of hydrogen generation.

processes change greatly with a change in the degree of subcooling.(39) Simultaneous differential equations to describe both the chemical and physical processes have been devised. The details of these equations and their solution on an electronic computer form the subject of a separate report.

Preliminary theoretical studies of these processes indicated that the reaction is initially controlled by the diffusion of water vapor through the hydrogen blanket surrounding the reacting particles.* At some later time, the buildup of a protective oxide film decreases the rate of solid-state processes such as ionic diffusion through the oxide lattice to a point where the reaction is no longer controlled by gaseous diffusion.

The partial pressure of water vapor at the surface between the liquid water and the vapor blanket surrounding the metal particle is the driving force for diffusion. The diffusion coefficient is, however, inversely proportional to the total pressure. Two extreme assumptions are possible. It might be supposed that the water surface reaches the boiling point. The vapor pressure is then equal to the total pressure at all times so that the diffusion rate is independent of pressure. It could also be assumed that the water surface remains at the bulk temperature of the water. In this case the diffusion rate could decrease markedly when either the pressure of inert gas or of hydrogen generated by reaction greatly exceeds the water vapor pressure. The data indicate that the latter assumption is more correct. Thus, reaction with room-temperature water is limited to a lower initial rate by gaseous diffusion processes. Runs with water vapor pressures of the order of one atmosphere or more were not significantly affected because the degree of subcooling was much less.

It is also possible, a priori, that the pressure effects were due to a sensitivity of the rate of solid-state processes to pressure. It seemed very unlikely, however, that pressure sensitivity would cease at about one atmosphere. Runs at pressures greater than one atmosphere did not lead to greater reaction.

The explosive pressure-rise rates observed above 2600 C were probably due to the ability of the metal particles to continue to subdivide under the influence of reaction-generated turbulence. Molten oxide would not form a rigid casing for the metal and fresh surface could form rapidly. Smaller particles lead to greatly increased rates of diffusion and cooling. Reaction would be much more rapid although not necessarily more extensive.

An interesting limitation to the extent of a metal-water reaction might result from the phenomenon of thermal diffusion. In the metal-water reaction, hydrogen (light molecule) must leave the hot surface and water vapor (heavy molecule) must approach the hot surface. The process is, therefore, opposed by thermal diffusion. Frank-Kamenetskii(31) points out that thermal diffusion can be very important in mixtures involving hydrogen when a steep temperature gradient is involved.

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* This view was also expressed by L. F. Epstein.(27)

## VII. DISCUSSION

Most fundamental studies of exploding wires have been confined to very fine wires and very powerful discharges.(33) These studies were generally aimed at producing exceedingly high temperatures in the study of plasma physics or to generate light flashes or magnetic fields of a tremendous magnitude. The present study is different in that research was directed toward heating a maximum quantity of metal to an accurately known temperature in a range of interest in chemical studies.

The two methods of energy measurement are believed to be unique in the field of exploding wires. The methods are not applicable, however, to very rapid discharges where the ac skin effect would prevent uniform heating of constantan wire elements. The methods presented seem well suited for chemical studies in which accuracy, simplicity, and reliability are more important than extreme heating rate. The calculated metal temperatures were presented to the nearest hundred degrees Centigrade or to the nearest ten percent melted. This was believed to represent the probably accuracy of the energy-measurement methods. The estimate of accuracy is born out by the results in several ways: (1) the correlation between calculated temperature and indications of melting for both zirconium and platinum, (2) reproducibility of the critical temperature between explosive and nonexplosive runs with zirconium, and (3) reproducibility of the observed extent of reaction.

Much of the scatter that is present in the plots of percent reaction vs. initial metal temperature is due to variations in the particle sizes generated by the discharge. This can be seen in Table 2, where a small mean particle diameter is generally associated with an increased extent of reaction. The irregularity in the particle diameters provided means of studying the effect of particle size. Particle size was varied at initial temperatures of the order of the melting point or less by varying the diameter of specimen wires. Differences in particle sizes from different wire diameters largely disappeared, however, when temperatures greatly exceeded the melting point.

The principal failings of the condenser-discharge method as employed by previous investigators, i.e., unknown initial temperatures and surface areas, have been corrected in large measure by methods developed in the present study. It has thus been possible to take advantage of the inherent simplicity of the method to study the zirconium-water reaction under a diversity of experimental conditions. Initial metal temperatures ranging from 1100 to over 4000 C and pressures ranging from 0.5 to over 200 psi have been studied. It should be possible to study reactions at pressures up to 1500 psi in the high-pressure cell without modification. Preliminary studies of the effect of inert gas pressure have also been completed.

The range of temperature and pressure studied by the condenser method could be reached by other methods only with great difficulty. Pouring or spraying methods require crucible heating, which ultimately involves some contamination of the metal. Difficulties of crucible heating to extreme temperatures and pressures are obvious. A method involving levitation melting has recently been demonstrated by Furman and McManus.(28) This method also provides metal which is free from contamination. It is possible, in principle, to vary temperature, pressure, and particle size independently. In practice, however, it is very difficult to devise induction coils that will levitate molten metal particles of varying sizes at varying temperatures.

## VIII. SUMMARY

A method of studying the reaction of molten metals with water was developed and preliminary results with zirconium reported. Rapid heating of metal wires to accurately known temperatures was accomplished by means of surge currents from a bank of condensers. Wires were normally heated to a final temperature in 0.3 msec. Two methods of determining the energy given to specimen wires were developed; these methods enabled calculation of metal temperature to within 100 C. Energy-measurement methods involved the use of short lengths of constantan wire with a small thermocouple attached to their outer surface. The wires were located in the discharge circuitry so that they were heated along with specimen wires. Temperatures reached by the wire elements were used to calculate values of the energy imparted to specimen wires. Accuracy of temperature calculation was verified by the agreement of calculated melting temperatures and physical indications of melting for two metals and two wire sizes. High-speed motion pictures indicated that uniform heating occurred and showed details of the process whereby liquefied metal wires disintegrated into spherical particles.

Details of the design of two reaction cells were presented. One cell was useful for runs at low pressures and the other could be used at high pressure with heated water. Means of collecting and measuring the quantity of hydrogen generated by reaction were developed, and the results were used to determine the extent of metal-water reaction. The rapidity of gas evolution was determined by means of a quartz crystal pressure transducer which retained a rapid response and high sensitivity at elevated ambient temperature and pressure. A simple optical method was used to obtain the mean particle diameter of the spherical particles obtained in runs with zirconium and platinum. Accurate determinations of initial metal temperature and of particle sizes corrected the principal failings of the method as employed by previous investigators.

The zirconium-water reaction was studied with initial metal temperatures from 1100 to over 4000 C with 30- and 60-mil diameter wires in water at room temperature and under an initial total pressure of *ca*. 0.5 psi.

Runs in the high-pressure cell were made with 60-mil wires through the melting point in water from room temperature to 200 C with corresponding pressures up to 225 psi. Results in room-temperature water showed that progressively greater reaction occurred at higher initial metal temperatures, reaching 20% reaction at 2600 C. Pressure traces showed that from one to several tenths seconds were required for reaction to reach a final value. At temperatures exceeding 2600 C, the reaction became violent, reaching 40 to 70% completed in a few milliseconds. Generally finer particles resulted from the explosive runs. The change in character of the reaction was attributed to the formation of molten oxide, $ZrO_2$ (2700 C), which did not stabilize large particles formed in early stages of the wire disintegration. Generally, twice as much reaction occurred with 30-mil wires as with 60-mil wires at temperatures in the melting region and below.

Runs in heated water gave more extensive reaction at temperatures in the melting point region, reaching 50% reaction for fully melted metal. The increased reaction was obtained with water heated to 100 C (15 psi water vapor pressure). Heating to 200 C (225 psi water vapor pressure), however, produced no additional reaction. This unusual pressure effect was attributed to an increased rate of diffusion of water vapor through the barrier of hydrogen surrounding reacting metal particles. At a later time the raction becomes controlled by solid-state processes occurring within the partly oxidized particles (parabolic or other rate law). Reaction rates controlled by gaseous diffusion are normally independent of pressure, but only if the effective water temperature at the surface between liquid water and the steam-hydrogen blanket remains at the boiling point determined by the ambient pressure. Experimental results indicate that it does not. Hydrogen generated by reaction, therefore, tends to suppress further reaction with water at room temperature. With heated water, the vapor pressure is more nearly equal to the total pressure at all times so that reaction is not suppressed.

Equations describing the reaction and cooling processes and their solution on an electronic computer will be presented in a separate report along with a quantitative comparison with experiment.

## IX. ACKNOWLEDGMENTS

The authors are indebted to C. H. Bean and the Metallurgy Division of ANL for preparation of the zirconium wires, and to H. H. Cremer and the Electronics Division of ANL for the design and construction of the condenser-charging and triggering circuitry.

## Appendix A

## SURVEY OF PREVIOUS STUDIES[a]

The purpose of this survey is to summarize and to criticize both the experimental methods that have been used to study metal-water reactions and the results of these studies. The results of this survey were used to select the experimental methods presently being used in the Chemical Engineering Division of ANL. Reports of research in this field that were published subsequently to the original preparation of this survey are briefly summarized in a closing paragraph.

The literature survey has been limited to zirconium, aluminum, uranium, stainless steel, and certain of their alloys which are normally used or considered as core materials for nuclear reactors. Studies dealing only with low-temperature steam corrosion have been omitted.

Molten metal-water reactions fall into the category of rapid chemical reactions. The most critical requirement of an experimental method to determine rates of reactions is that the reactants must be brought together in a time which is short compared to the period of observation. Either of two methods may then be used to follow the reaction. Some index of the extent of reaction can be measured continuously as a function of time, or the reaction can be quenched after a period of time and the extent of reaction determined.

It is often impossible to carry out rapid reactions under isothermal conditions. A given experimental method must then be evaluated in terms of how well reaction temperature is controlled. Molten metal-water reactions are heterogeneous, so that the control of interfacial area must also receive important consideration.

In addition to the controls that the experimental method imposes on the reaction, it is necessary to consider what measurement techniques are used to define the reaction conditions of temperature and pressure and to follow the extent of reaction. The measurement techniques must be judged in terms of their accuracy and time response.

The experimental methods that have been used can be divided into six broad categories as follows:

1. pouring or spraying molten metal into water;
2. molten metal drops falling into water;
3. dispersion of molten metal by an explosive charge;

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[a] Presented originally as part of an internal ANL report on April 1, 1958 by L. Baker, Jr., and C. H. Smith and reproduced by R. O. Brittan as part of Ref. 32.

4. slow heating of metal immersed in water or steam;
5. in-pile heating in MTR; and
6. dispersion of metal by a condenser discharge.

Each category will be discussed separately. A final summary of results is included.

## 1. Pouring or Spraying Molten Metal into Water

### References

Aerojet General Corporation(1,2,3)
Aluminum Company of America(4,5,6)
Argonne National Laboratory(7)
Mine Safety Appliances(8-12)

### Method

Heating - Bulk metal samples were heated in crucibles.

Contacting - The metals were sprayed(3) or poured into liquid water.

Time of Heating or Contacting - There is reason to believe that traces of air or water vapor were in contact with the bulk melt for extended periods of time; however, the principal contact between fresh metal surface and water is made as the stream breaks up beneath the water surface. Contacting time for most of the surface is, therefore, very small.

Reaction Temperature - The initial temperatures of the molten metals were accurately known. Rapid cooling occurred in every case; however, no attempts were made to estimate or measure the cooling rates.

Interfacial Area - Accurate estimates were obtained(3) for the spray-formed spherical particles that were not entirely oxidized. It was assumed that the initial particle size did not change throughout the reaction. Measurement of particle size thus led to an estimate of the total interfacial area. The other experiments did not produce well-defined particles, so that no accurate estimate of the area was possible.

### Results

### Aluminum

a. Aluminum Company data(4,5,6) showed that explosions sometimes occurred when 50-lb batches of aluminum were discharged into water. Conditions leading to explosion are summarized as follows:

1. crucible exit hole diameter must be greater than $2\frac{3}{4}$ inches;
2. metal drop distance must be less than 10 ft;
3. water depth must be less than about 30 in. and more than one inch.

Paint or grease on the bottom of the water container was effective in preventing explosions. The authors concluded that aluminum-water reactions were not involved. The observations were explainable in terms of the rapid generation of steam. The absence of a flash indicated also that the $H_2$-$O_2$ reaction was also not involved.

b. Argonne(7) found no reactions and very minimal steam production using fine jets of molten metal.

c. Aerojet(1,2) and Mine Safety Appliances(8-12) found no reaction when molten aluminum was dropped into water without additional dispersion by a blasting cap.

d. Aerojet(3) in the "explosion dynamometer" obtained negligible reaction below 1200 C. Above an initial metal temperature of 1200 C, evidence of strong reaction was obtained. The 1200 C temperature was beyond the range of any of the other investigators who used pouring methods. Aluminum at 2070 C gave a stronger pressure pulse than zirconium, stainless steel, NaK, or black powder.

## Zirconium

a. Aerojet(1,2) found black glass-like coatings (0.005 in. thick) after pouring 454 gm of molten Zr into water. Calculations, considering the film thickness and an average droplet size, indicated that 16 percent of the metal was oxidized before the metal was quenched.

b. Aerojet(3) in the "explosion dynamometer" (spraying) found that strong explosions occurred with zirconium over the temperature range from 1900 to 2600 C. There was no clear-cut effect of temperature. The individual drops were collected and the thickness of the oxide layer determined. The extent of reaction varied from complete for small (10-20 micron) drops to about 50 percent for 100-micron drops and to about 20 percent for 1000-micron drops. These results are approximately what one would obtain if 25 microns of metal had reacted uniformly from the surface of each drop.

c. Mine Safety Appliances(8-12) found that zirconium reacted up to 60 percent in 750 psi steam and to a lesser extent at lower pressures. Considerably less reaction was noted when the zirconium was dropped into room-temperature water.

Zircaloy-2 and Zirconium + 1% Beryllium - Results were identical to zirconium within the experimental error.(3)

Stainless Steel, Type 303 - One run was reported in the Aerojet explosion dynamometer(3) in which a strong reaction was reported at 2270 C.

Nickel - Nickel at 1900 C gave essentially no reaction in the explosion dynamometer. This observation constituted an important verification of the method.

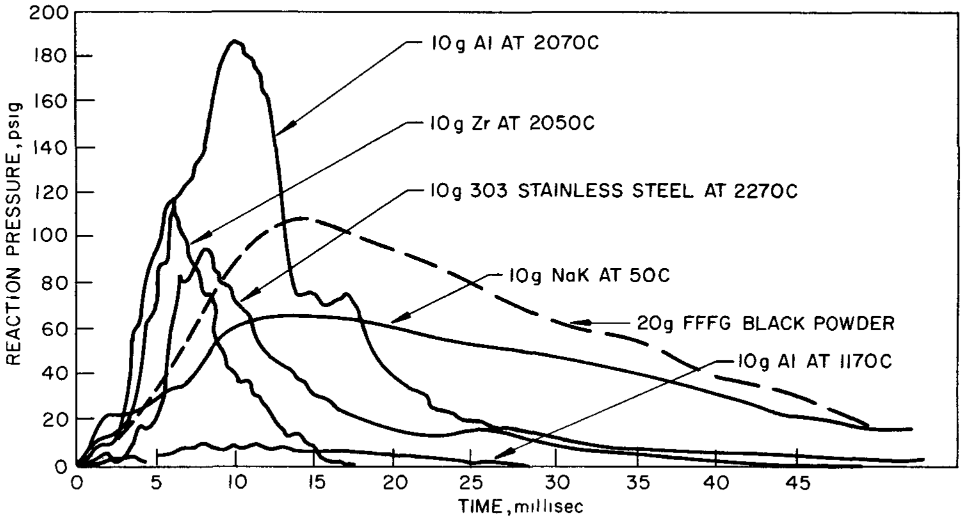
Uranium - A single measurement in the explosion dynamometer of uranium at 1766 C showed that a very mild reaction occurred.

## Discussion of Results

The results obtained with the explosion dynamometer are qualitative in nature. The nature and rapidity of the reactions are illustrated in Figure 21. The rate of rise of the pressure is necessarily limited by the rate of injection of the molten metal, so that even faster rections are likely to occur under different conditions. In spite of the apparent violence of the reactions, it seems well established that the reactions are not self-sustaining and do not go to completion. It was also likely that no hydrogen-oxygen reaction was involved since "de-gassed" water was used and no air space was available to the hydrogen.

Figure 21

RESULTS OF AEROJET EXPLOSION DYNAMOMETER TESTS(3)



## 2. Molten Metal Drops Falling into Water

### References

Battelle Memorial Institute(13)

### Method

Heating - One end of a supported rod was heated inductively until a single drop fell.

Contacting - The drop fell through an inert atmosphere into a water vapor-argon mixture and finally into a 25-ft column of liquid water.

Time of Heating or Contacting - The metal was probably in contact with some water vapor during the entire heating operation. It was only in contact with nearly pure steam for about 50 msec while in flight before entering the liquid.

Reaction Temperature - The initial temperature of the metal was presumed to have been the melting point. The time of fall through the water column required to quench luminosity was recorded. If it could be assumed that the end of luminosity corresponded to a definite temperature, then a qualitative time-temperature history was obtainable.

Interfacial Area - The use of single drops made accurate area estimations possible. The drops after reaction had a characteristic cup-shaped indentation on one side, which complicated the situation.

### Results for Zirconium

a. The time to the end of luminescence rose from 2 to 10 sec as the initial water temperature was raised from 90 to 200 F. The corresponding depth of fall through the water ranged from 8 to 24 ft.

b. It was found that 39 to 45 percent of the zirconium in nominal 0.2-in. drops reacted, although no particularly rapid or explosive reactions occurred.

c. The observed thicknesses of oxide layer corresponded approximately to those extrapolated from rate data for solid metal-steam reactions.

### Discussion of Results

The fact that the drops initially were at the melting point and possibly not fully melted could mean that the drop surfaces were molten for only a short time. This severely limits the value of the data.

## 3. Dispersion of Molten Metal into Water by an Explosive Charge

### References

Aerojet General Corporation(1,2,3)

### Method

Heating - An induction furnace was used to melt the sample to be studied in a bottom-tapped crucible.

Contacting - The sample was dropped into the water as soon as possible after reaching the melting temperature. The molten metal was dispersed by a blasting cap aligned directly beneath the outlet of the crucible and mounted 5 in. below the surface of the water. Protection of the metal from premature oxidation was done by a purified argon gas blanket during the heating cycle.

Time of Heating or Contacting - The molten metal stream was dispersed into the water instantaneously by the explosive charge.

Reaction Temperature - The temperature of the melt was measured, but the reaction temperature could be determined only from a heat balance. It depends upon the heat loss rates from the metal to the surrounding water and upon the rate of chemical reaction.

Interfacial Area - Particle-size analyses of the recovered residue were made. Measurements were made, using a filar eyepiece in the metallograph, of the thickness of the oxide layer and the diameter of the metallic core. These measurements determined the original droplet diameters before oxidation.

### Results

#### Aluminum

a. There was very little reaction when molten drops at 900-1000 C were comparatively large. However, the estimated percentage of reaction was 75 percent at a temperature of about 1565 C when the metal was dispersed.

b. The importance of temperature was shown. Aluminum was found to be essentially nonreactive at 930 C, but reacted explosively at 1565 C.

### Uranium

a. The residue was found to be partially atomized (approximately 8 percent by weight for particles less than 140 microns in diameter), but the bulk remained as large, irregular platelets covered with a surface oxidation.

b. The percentage of reaction varied from 30 to 50 percent. There were indications of slight explosions in a few of the tests.

c. The reaction of molten uranium with water was generally not violent or self-sustaining at a temperature of 1540 C.

### Zirconium

a. All or nearly all of the metal reacted violently in every case.

b. For one particular case, sparks were thrown 50 ft into the air. The temperature was approximately the melting point of zirconium (1840 C). From the equipment damage, a stress calculation indicated that a pressure of at least 2200 psi would be necessary to produce the effects noted. Then assuming 100 percent reaction, the 454 gm of zirconium produced 235 liters of hydrogen and released 214 kcal of heat.

### Discussion of Results

The validity of using a blasting cap for dispersal of the molten metal was obtained by comparing drop tests runs with the explosion dynamometer (spraying) test runs. The curves were similar, and it was concluded that the energy added by the blasting cap (800 cal) was minor. It was hypothesized from this that all mechanisms for obtaining the dispersion of molten metal would probably lead to the same results, assuming an identical particle size distribution.

## 4. Induction Heating of Metal Immersed in Water or Steam

### References

Battelle Memorial Institute(13)

WAPD(14)

### Method

Heating - An induction furnace was used to heat a supported solid Zircaloy-2 sample(13,14) and to heat a molten Zircaloy-2 sample contained in a graphite crucible.(13)

Contacting:

a. The specimens were mounted inside a Vycor Tube and protected by an argon gas blanket during the heating period. When the solid sample reached the reaction temperature, 50 psia steam was passed through the reactor, and when the molten sample reached the reaction temperature, a jet of 50 psia steam was directed upon the surface of the molten Zircaloy-2.

b. The samples were heated to the desired temperature in an initial water atmosphere.(14)

Time of Heating or Contacting:

a. Steam was present in the solid sample system for 0.08 to 120 min and was present in the molten sample system for 1 to 25 sec.(13)

b. The sample was heated to the desired temperature in 5 to 10 sec. The contacting period was the time required to collect successive 250-ml volumes of hydrogen, and the time periods were from 10 sec up to 55 min.(14)

Reaction Temperature:

a. The temperatures of the solid specimens and of the melts were measured initially. There is some doubt as to what the reaction temperature was because of the rapid chemical reactions of the steam with the molten samples and because of the increased heat losses from the solid sample with a steam surroundings rather than an argon gas atmosphere.(13)

b. The sample temperature tended to remain constant during the reaction period and ranged from 1300 to approximately 1860 C.

Interfacial Area - Initially the interfacial areas for both solid and molten samples were known accurately. The interfacial area of the sample during melting was probably quite different from the initial area.(14)

## Results

### Zircaloy-2

Battelle Memorial Institute(13)

a. Reactions below 1690 C and reaction times between 5 sec and 2 hr were best correlated as

$$v^2 = 0.1132 \times 10^6 \, \theta \exp[(-34{,}000 \pm 1440)/RT] \quad ,$$

with v in units of ml of hydrogen per square centimeter and $\theta$ in units of seconds.

b. The reaction rate between molten Zircaloy-2 and steam did not correlate with the initial metal temperature. However, the reaction rates were higher than those predicted from the extrapolation of result a.

c. Pressure appeared to have little effect between 20 and 50 psia.

d. Between 4 and 13 percent of the hydrogen formed in the reaction of steam with Zircaloy-2 was absorbed in the sample.

e. As the reaction temperature was increased, the ratio between the thickness of the zirconia layer and the alpha-phase layer decreased.

WAPD(14)

f. Reaction rates were fast at the temperatures used, but were not explosive or violent even at temperatures above the melting point.

g. The oxidation rates of Zircaloy-2 near its melting point in water were approximately the values that would be obtained from the extrapolation of the oxidation of zirconium in air data.

h. The scales formed during the oxidation were essentially the same in appearance and order of formation as those formed during the scaling of zirconium in oxygen.

i. Small amounts of uranium and boron did not affect the high-temperature oxidation rates of Zircaloy-2 in water.

### Discussion of Results

The reaction rate data from Battelle(13) for Zircaloy-2 steam were lower than WAPD data(14) for reaction rates between Zircaloy-2 and water at the same duration and temperature. The Battelle data are probably lower because of the uncertainty of the reaction temperature. The comparative data imply that the WAPD reaction mechanism is a metal-steam reaction.

### 5. In-pile Heating in MTR

### References

Phillips Petroleum Company(15,16,17)
Westinghouse(18,19)

Method

Heating - The metal under study was either alloyed with $U^{235}$ or formed as a clad around $U^{235}$ fuel, placed in an autoclave, and then immersed in the MTR reactor for a specified period of time (6-15 sec).

Contacting - The metal was either surrounded by water the entire time or surrounded by water vapor and allowed to flow or drip into liquid water.

Time of Heating or Contacting - It was estimated to require 0.1-0.2 sec to reach the melting point.(12) Heating continued, however, for the entire period of immersion.

Reaction Temperature - The temperature could be determined only from a heat balance. It depends upon heat loss rates from the metal to the autoclave materials and upon the rate of chemical reaction.

Interfacial Area. The interfacial area was largely unknown.

Results

Aluminum

a. Samples that did not melt gave no reaction.

b. Molten samples reacted.

c. Sporadic explosions were obtained only with samples that reached temperatures slightly above the melting point.

Zirconium

a. Molten samples gave reactions up to 80 percent completion, with some sporadic explosions.

Nichrome

a. Molten samples gave up to 30 percent reaction with sporadic explosions.

Discussion of Results

a. The sporadic explosions and pressure surges may have been due entirely to localized overheating and the release of gas pockets. It is not at all certain that the apparent pressure transients are related to metal-water reactions. It is also likely that some of the transients were due to electrical disturbances, since the authors report considerable difficulty with the instrumentation.

### 6. Dispersion of Metal by a Condenser Discharge

References

Argonne National Laboratory(20)
Bureau of Mines(21)
Columbia University(22,23)
KAPL(24)
Atomics International(25,26)
Fundamentals of fusing wires(38,40,41,42,43)

Method

Heating - The metal under study is in the form of a wire or ribbon and is heated rapidly to virtually any desired temperature by a momentary surge current from a bank of condensers or from a short-circuited dc generator.(22,23)

Contacting - The wire or ribbon is immersed in either steam or water throughout the heating process.

Time of Heating or Contacting - A considerable range can be achieved by variation of the electrical parameters in the discharge circuit.

a. Several studies of exploding wires as high-intensity light sources(41,42) and fundamental studies of the physics of the disintegration process(38,40,43) have used very short heating periods (1-10 $\mu$sec).

b. Periods of the order of 100 $\mu$sec were used by several investigators to study metal-water reactions.(20,21,26)

c. Slow discharges (3-50 msec) were used(22,23,24) to study metal-water reactions.

Reaction Temperature

a. Rapid heating methods (1-100 $\mu$sec) have produced temperatures up to 100,000 C.

b. Slow heating methods (3 msec or longer) are limited to the melting points of the metals, since electrical contact is broken.

Interfacial Area - The particle size probably depends on the rate of heating, the amount of energy supplied, and the wire diameter.

a. Rapid heating and high energies - the metals or metal oxides were reduced to colloidal particles.(20)

b. Rapid heating and low energies - A mixture of fine and coarse particles was obtained.(21,26)

c. Slow heating (20-50 msec) and moderate energy input(24) gave coarse particles. Energy inputs below that required for complete fusion caused the wire to part in only a few places.

### Results

#### Aluminum

a. Plott(20) concerned himself exclusively with aluminum. It would appear that he obtained complete reaction in every run; however, he used more than sufficient energy to vaporize the metal. His results thus are of little use in evaluation kinetics of molten metal-water reactions.

b. Data from Atomics International(26) for percent reaction as measured by hydrogen evolution as a function of the energy input were presented in tabular form. The values of energy input are subject to considerable uncertainty. It appears that significant reaction occurs only when enough energy is used to melt the metal.

c. Columbia University results(23) indicated that aluminum is nonreactive at the melting point.

Aluminum + 3.5% Lithium Alloy - Data from Atomics International(26) make it appear that the addition of lithium suppressed the reaction. This conclusion cannot be accepted without further proof. It is likely that more uncertainty exists in the energy input calculation in the case of the alloy since the electrical resistivity may not be known accurately.

#### Zirconium

a. Data from Atomics International(26) lead one to the conclusion that molten zirconium will react extensively under these conditions.

b. KAPL,(24) using the slow discharge method, found that large zirconium pieces and the balled ends of the wire continued to "burn" for some time after completion of the energy pulse.

c. Columbia University(23) reported that a water reaction with zirconium occurred during the 0.8 to 2 msec required to quench glowing fragments. A tendency to self-sustained reaction was noted.

#### Uranium

a. The data of Atomics International(26) indicated that appreciable reaction could occur.

b. Columbia University(23) reported that no evidence of self-sustained reaction was found.

## Discussion of Results

The data of Atomics International(26) are the only quantitative metal-water reaction data that have been obtained by the condenser-discharge method. No attempt was made to obtain rate data as distinguished from measurements of the extent of reaction. Extent of reaction data, however, can be used to estimate rates if estimates of the total surface area and the quenching time can be made.

The work of Atomics International(26) is an excellent beginning to the study of metal-fluid reactions. Work is required to improve the accuracy of the measurement of energy input and particle size. Transient pressure and temperature measurements are required to obtain rate data.

## Summary of Results

### Aluminum

The only reports of aluminum reactivity at or slightly above the melting point resulted from the in-pile measurements and from the exploding wire studies of Ruebsamen et al.(25,26) In both cases, only crude estimates of temperature could be made. The reported pressure surges obtained with aluminum in the in-pile studies were not necessarily indicative of aluminum-water reaction. The pouring and spraying experiments indicated strongly that aluminum below about 1200 C does not react appreciably. The explosion dynamometer work and the experiments with explosive dispersion showed that aluminum reacts strongly above 1200 C. Aluminum at 2070 C gave a stronger explosion on being sprayed into water than did an equal quantity of zirconium at the same temperature.

### Uranium

The data for uranium are much more limited than those for aluminum or zirconium. Indications are that only surface corrosion occurs at temperatures up to 1700 C. Only mild reaction was noted in the explosion dynamometer and explosive charge methods. The exploding-wire experiments show that uranium can react almost completely if a high degree of subdivision is obtained.

### Stainless Steel

A single experiment in the explosion dynamometer indicated that stainless steel was similar to zirconium in its behavior toward water.

### Zirconium (Zircaloy):

The data and studies have shown that solid Zircaloy-2 follows the parabolic law approximately for reaction with both liquid water and steam up to the melting point. The reaction with water (steam layer) is somewhat more rapid than that with steam; however, neither is very rapid nor violent. No evidence was reported in any of the studies of an ignition followed by rapid consumption of the metal, such as occurs with most metals in oxygen. All of the data, including the exploding wire studies, the single drop experiments, and the pouring and spraying work, are consistent with the idea that rates of the molten metal reactions at temperatures above the melting point may be obtained qualitatively by extrapolating the low-temperature data obtained with solid specimens. The relatively greater reaction obtained by the spraying, explosive dispersion, and exploding wire methods are probably due only to the greater interfacial area for reaction.

## Recent Studies

Several experimental investigations in the field of metal-water reactions have been reported since early 1958. Two reports, one by S. C. Furman(27) and another by S. C. Furman and P.A. McManus,(28) summarize experimental studies conducted by the General Electric Atomic Power Equipment Department. In the first of these, sodium, aluminum, and zirconium were reacted with dilute water vapor in one atmosphere of helium. The second was a feasibility study of two techniques of potential value in metal-water studies. One of these was the suspension of molten metal samples by electromagnetic levitation and the other involved the use of a high-speed infrared pyrometer.

Studies of the reaction of molten aluminum and aluminum-uranium alloys with water vapor were reported by W. F. Zelezny of Phillips Petroleum Atomic Energy Division.(29) The molten metals, contained in crucibles, were exposed to water vapor while suspended from a recording thermobalance.

## Appendix B

## THEORY OF THE DISCHARGE CURRENT

The transient current when a charged condenser is suddenly connected to a circuit containing only resistance and inductance is shown in standard texts* on electricity to have the following form:

$$i = \frac{V}{\sqrt{\frac{L}{C} - \frac{R^2}{4}}} \exp\left(-\frac{R}{2L} t\right) \sin\sqrt{\frac{1}{LC} - \frac{R^2}{4L^2}} \; t \quad , \qquad B(1)$$

so long as the following applies:

$$R^2 < \frac{4L}{C} \qquad B(2)$$

where:

$i$ is current in amp,

$V$ is initial charging voltage,

$R$ is total circuit resistance in ohms,

$L$ is total circuit inductance in henries,

$C$ is capacitance in farads, and

$t$ is time in sec.

The total circuit resistance $R$ is the sum of the specimen wire resistance, $R_1$ in Figure 1, and the extraneous resistance $R_e$. For the alternative circuit in Figure 1, the total circuit resistance $R$ has the following value:

$$R = R_e + \frac{R_1 \; R_2}{R_1 + R_2} \quad .$$

The ranges of circuit constants used during the experiments were as follows:

$C$ - 24.8 to 99 $\mu$farad,

$L$ - 2.5 $\mu$henry,

$R_e$ - 0.04 ohm,

$R_1$ - 0.006 to 0.1 ohm,

$R_2$ - 0.03 to 0.3 ohm.

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*For example, see Reference 44.

The largest total $R^2$ used was less than 10% of 4 L/C, so that Equation B(1) can be expressed approximately as follows:

$$i = V\sqrt{\frac{C}{L}} \exp\left(-\frac{R}{2L} t\right) \sin\sqrt{\frac{1}{LC}} t \quad . \qquad B(3)$$

The frequency of the oscillatory discharge, f, the period of a current half-cycle, $t_{1/2}$, and the peak instantaneous current $i_{max}$ follow from Equation B(3):

$$f, \sec^{-1} = \frac{1}{2\pi\sqrt{LC}} \quad , \qquad B(4)$$

$$t_{1/2}, \sec = \pi\sqrt{LC} \quad , \qquad B(5)$$

$$i_{max} \simeq V\sqrt{\frac{C}{L}} \quad . \qquad B(6)$$

The circuit inductance L can be obtained most easily from the current oscillogram by means of Equation B(6). Figure 2 is a typical current oscillogram of a discharge through a 64-mil nichrome wire. The period of a half cycle in Figure 2 is 0.050 msec; since C was 99 $\mu$farad, L was 2.5 $\mu$henries. It follows from Equations B(3), B(4), and B(6) that the oscillation frequency and the maximum current are relatively independent of the circuit resistance.

## Appendix C

## ANALYSIS AND CALIBRATION OF THE TWO-COUPLE ENERGY-MEASUREMENT CIRCUIT

A circuit diagram is shown in Figure 1. The parallel current paths containing the specimen wire resistance $R_1$ and the resistor $R_2$ are both considered purely resistive. Consider, first, the energy distribution between the combined resistance $R_1$ and $R_2$ and the extraneous resistance $R_e$. The equivalent resistance $R_{eq}$ of the parallel combination of $R_1$ and $R_2$ is

$$R_{eq} = \frac{R_1 R_2}{R_1+R_2} \quad . \qquad C(1)$$

Since $R_{eq}$ is in series with $R_e$, the energy distribution is

$$\frac{E_1 + E_2}{Ee} = \frac{R_1 R_2}{R_e (R_1 + R_2)} \quad . \qquad C(2)$$

It is now necessary to consider the energy distribution between elements in parallel:

$$\frac{E_1}{E_2} = \frac{R_2}{R_1} \quad . \qquad C(3)$$

It was shown in Chapter IV, Section A3, that the energy absorbed by a circuit element is its resistance times the action integral:

$$Ee = R_e S_1 \text{ and } E_2 = R_2 S_2 \quad . \qquad C(4)$$

The action integrals are also expressible in terms of a calibration factor k and the observable temperature rise $\Delta T$:

$$S_1 = \Delta T_1/k_1 \quad , \quad S_2 = \Delta T_2/k_2 \quad . \qquad C(5)$$

Equations C(1) thru C(5) can be combined to yield the following results. The energy absorbed by both $R_1$ and $R_2$ is

$$E_1 + E_2 = R_2 \sqrt{k_1 k_2} \sqrt{\Delta T_1 \Delta T_2} \quad , \qquad C(6)$$

the energy absorbed by the specimen wire alone is

$$E_1 = R_2 \sqrt{k_1 k_2} \sqrt{\Delta T_1 \Delta T_2} \left( 1 - \sqrt{\frac{k_2 \Delta T_2}{k_1 \Delta T_1}} \right) \quad , \qquad C(7)$$

and the value of $R_1$, the specimen wire resistance, is

$$R_1 = \frac{R_2\sqrt{\frac{k_2}{k_1}\,\frac{\Delta T_2}{\Delta T_1}}}{1 - \sqrt{\frac{k_2}{k_1}\,\frac{\Delta T_2}{\Delta T_1}}} \quad . \qquad C(8)$$

The calibration procedure employed to determine numerical values of $R_2$, $k_1$, and $k_2$ involves three series of discharges. It was found useful to use a 14 gauge nichrome wire for a series of moderately powerful discharges. The nichrome wire was able to absorb considerable energy without being destroyed. The total energy given to the nichrome and to the shunt path resistor $R_2$ were determined for each discharge by Method I described in Chapter IV, Section A3. The energy stored in the condensers was considered divided into two parts instead of three. This method involves a series of short-circuited discharges in the preparation of a plot of the type shown in Figure 4. The energy values and the observed temperature rises were then used to evaluate the combined constant $R_2\sqrt{k_1 k_2}$ by means of Equation C(6). Typical results of such a calibration are shown in Table 4.

Table 4

DETERMINATION OF CALIBRATION CONSTANTS, METHOD II, $R_2$ = 0.0279 OHM

| $E_1 + E_2$, by Method I (cal) | Temp Rise (C) | | $\sqrt{\Delta T_1\ \Delta T_2}$ | Constant $R_2\sqrt{k_1 k_2}$ (cal) |
|---|---|---|---|---|
| | $\Delta T_1$ | $\Delta T_2$ | | |
| 6.9 | 16.2 | 13.8 | 15.0 | 0.460 |
| 10.1 | 24.4 | 20.8 | 22.5 | 0.446 |
| 14.5 | 34.3 | 29.9 | 32.1 | 0.451 |
| 16.1 | 39.2 | 33.9 | 36.5 | 0.440 |
| 19.5 | 46.3 | 41.1 | 43.6 | 0.447 |
| 19.8 | 46.0 | 41.3 | 43.6 | 0.454 |
| 16.4 | 39.0 | 34.1 | 36.5 | 0.449 |
| 13.8 | 34.8 | 30.0 | 32.3 | 0.426 |
| 10.6 | 24.2 | 21.0 | 22.6 | 0.468 |
| 6.9 | 16.2 | 13.7 | 14.9 | 0.464 |
| | | | | Avg 0.450 ± 0.012 |

Another sequence of discharges is then performed with no specimen or shorting bar in place. Equation C(7) shows that under open-circuit conditions and with $E_1 = 0$.

$$\Delta T_2/\Delta T_1 = k_2/k_1 \quad . \qquad C(9)$$

This expresses the fact that the same current now flows through both thermoelements. The results of a series of open-circuit discharges are shown in Table 5. The accuracy of determination of $k_2/k_1$ is somewhat reduced because the two elements are not generally of similar size. A powerful discharge is likely to destroy thermoelement 2 while a very weak discharge will result in only slight heating of thermoelement 1. The selection of element sizes in relation to the calibration problem and in relation to the size of specimen wires to be heated must be considered together in the original circuit design. A diameter ratio of 2:1 for the constantan wires in the thermoelements was found very satisfactory.

Table 5

DETERMINATION OF CALIBRATION CONSTANTS BY OPEN-CIRCUIT DISCHARGE, METHOD II

| Temp Rise (C) | | $k_2/k_1$ |
|---|---|---|
| $\Delta T_1$ | $\Delta T_2$ | |
| 8.3 | 56.1 | 0.148 |
| 9.5 | 68.8 | 0.138 |
| 11.2 | 83.4 | 0.134 |
| 11.7 | 83.4 | 0.140 |
| 9.5 | 69.4 | 0.137 |
| 8.0 | 56.6 | 0.141 |
| | | Avg 0.140 ± 0.004 |

The foregoing procedures provide sufficient information to use Equation C(7) for the determination of the energy absorbed by specimen wires. Determination of the specimen wire resistance $R_1$ by Equation C(8), however, requires an independent value of $R_2$. The resistance $R_2$ was constructed of a single straight length of constantan wire so that its resistance was independent of temperature and constant throughout a discharge; its value was readily determined by passing a steady current from a 12-volt storage battery through a calibrated 1-ohm resistor and through $R_2$ in series with about 100 ohms. The voltage developed across the 1-ohm resistor and $R_2$ were then measured with a millivolt potentiometer. Resistance values could be measured to an accuracy of 0.0001 ohm in this manner.

A series of three overall calibrations were performed to show that the constants obtained were independent of oscillation frequency. The frequency was varied by varying the number of condensers. The results obtained in the three series of calibrations are shown in Table 6.

Table 6

COMPARISON OF CALIBRATION CONSTANTS OBTAINED AT DIFFERENT FREQUENCIES; $R_2 = 0.0486$ ohm

| Number of Condensers | Frequency (cycles/sec) | $\sqrt{k_1}$ | $\sqrt{k_2}$ | $\sqrt{\frac{k_2}{k_1}}$ | $R_2\sqrt{k_1 k_2}$ |
|---|---|---|---|---|---|
| 1 | 20,000 | 5.86 | 2.53 | 0.431 | 0.721 |
| 2 | 14,000 | 5.56 | 2.66 | 0.477 | 0.719 |
| 4 | 10,000 | 5.74 | 2.78 | 0.485 | 0.775 |

# REFERENCES

1. H. M. Higgins, A Study of the Reaction of Metals and Water, AECD-3664 (April 1955).
2. H. M. Higgins, The Reaction of Molten Uranium and Zirconium, AGC-AE-17 (April 1956).
3. H M. Higgins and R. D. Schultz, The Reaction of Metals in Oxidizing Gases at High Temperatures, IDO-28000 (April 1957).
4. G. Long, P. T. Stroup, and W. T. Ennor, Explosions of Aluminum and Water, NP-5471 (Aug 1950).
5. G. Long, Explosions of Molten Aluminum in Water, Cause and Prevention, Metal Progress 71, 107 (1957).
6. A. S. Russell, Aluminum Water Explosions, Memo, Aluminum Company of America, New Kensington, Pa. (April 1950).
7. J. M. West and J. T. Weills, Reactor Engineering Division Quarterly Report, September 1, 1950 through November 30, 1950 ANL-4549 (Dec 1950).
8. W. Milich and E. C. King, Molten Metal-Water Reactions, NP-5813, Tech. Rpt. No. 44 (Nov 1955).
9. J. W. Mausteller, ed., Progress Report No. 27 for February and March 1955, NP-5601 (April 1955).
10. J. W. Mausteller, ed., Progress Report No. 28 for April and May 1955, NP-5690 (June 1955).
11. J. W. Mausteller, ed., Progress Report No. 29 for June and July 1955, NP-5739 (August 1955).
12. W. J. Posey, ed., Progress Report No. 30 for August and September 1955, NP-5779 (Oct 1955).
13. A. W. Lemmon, Jr., Studies Relating to the Reaction between Zirconium and Water at High Temperatures, BMI-1154 (Jan 1957).
14. W. A. Bostrom, The High Temperature Oxidation of Zircaloy in Water, WAPD-104 (March 1954).
15. O. J. Elgert, A Proposal for Aluminum Water Reaction Experiments in the MTR, IDO-16141 (Dec 1953).
16. O. J. Elgert, T. J. Boland, and G. L. Smith, Status Report Aluminum Water Reaction Experiment, PPC-89 (March 1955).
17. O. J. Elgert and A. W. Brown, In-pile Molten Metal-Water Reaction Experiments, IDO-16257 (June 1956).

18. W. N. Lorentz, Chemical Reaction of Zirconium-Uranium Alloys in Water at High Temperatures, WAPD-PM-22 (del.) (July 1955).

19. W. F. Witzig, Short Time Autoclave Tests in the MTR, WAPD-P-513 (Sept 1954).

20. R. F. Plott, Reactions Produced by the Electrical Explosion of a Metal Immersed in a Fluid, ANL-5040 (Dec 1950).

21. J. A. Herickes, P. A. Richardson, M. Weiss, and G. Gelernter, Zirconium Hazards Research, September 1, 1956 through August 31, 1957, AECU-3642, Summary Report No. 3655, Bureau of Mines (Aug 1957).

22. M. Markels, Jr. and W. A. Stark, Fast Transient Heat Transfer in a Clad Element Stagnant Water System, TID-7529 (Part I) (Sept 1956).

23. A. J. Bendler, J. K. Raros, and N. H. Wagner, Fast Transient Heating and Explosion of Metals under Stagnant Liquids, AECU-3623 (CU-1-58-At-187-ChE) (Feb 1958).

24. D. C. Layman and H. L. Mars, Some Qualitative Observations of the Zirconium-Water Reaction at Atmospheric Pressure KAPL-1534 (April 1956).

25. W. C. Ruebsamen and J. B. Chrisney, Metal-Water Explosions, NAA-SR-Memo-75 (July 1951).

26. W. C. Ruebsamen, F. J. Shon, and J. B. Chrisney, Chemical Reaction Between Water and Rapidly Heated Metals, NAA-SR-197 (Oct 1952).

27. S. C. Furman, Metal-Water Reactions: V. The Kinetics of Metal-Water Reactions - Low Pressure Studies, GEAP-3208 (July 1959).

28. S. C. Furman and P. A. McManus, Metal-Water Reactions: IX. The Kinetics of Metal-Water Reactions - Feasibility Study of Some New Techniques, GEAP-3338 (Jan 1960).

29. W. F. Zelezny, Metal-Water Reactions: Rates of Reaction of Aluminum and Aluminum-Uranium Alloys with Water Vapor at Elevated Temperatures, IDO-16629 (Nov 1960).

30. J. R. Dietrich, Experimental Investigation of the Self-limitation of Power during Reactivity Transients in a Subcooled, Water-moderated Reactor, Borax-I Experiments, 1954, AECD-3668.

31. D. A. Frank-Kamenetskii, Diffusion and Heat Exchange in Chemical Kinetics, Princeton University Press, Princeton, N. J. (1955).

32. R. O. Brittan, Reactor Containment Including a Technical Progress Review, ANL-5948 (May 1959) pp. 145-160.

33. W. G. Chace and H. K. Moore, ed., Exploding Wires, Plenum Press, Inc., New York (1959).

34. E. H. Cullington, W. G. Chace, and R. L. Morgan, Low Voltage Trigger, Electronics (engineering edition) 31 (No. 15), 86 (1958).

35. J. H. Park, Shunts and Inductors for Surge-current Measurements, J. Research, NBS, 39, 191 (1947).

36. J. Tyroler, A Self-calibrating High Speed Photographic Pyrometer, "Sixth Symposium (International) on Combustion," Reinhold Corp., New York (1957), p. 763.

37. B. Lustman and F. Kerze, Jr., ed., The Metallurgy of Zirconium, McGraw-Hill Book Co., Inc., New York (1955).

38. I. F. Kvartskhava et al., Electrical Explosions of Metal Wires, Soviet Physics, JETP, 3, 40 (1956).

39. J. W. Westwater, "Boiling of Liquids" in Advances in Chemical Engineering, Academic Press Inc., N. Y., (1956) Vol. I, p. 1 ff.

40. V. V. Bondarenko et al., Resistance of Metals at High Current Densities, Soviet Physics, JETP, 1, 221 (1955).

41. J. A. Anderson, The Spectrum of Electrically Exploded Wires, The Astrophysical J. 51, 37 (1920).

42. J. A. Anderson and S. Smith, General Characteristics of Electrically Exploded Wires, The Astrophysical J. 64, 295 (1926).

43. A. E. Barrington, The Fusing of Wires with Heavy Surge Currents, Brit. J. App. Phys. 7, 408 (1956).

44. G. P. Harnwell, Principles of Electricity and Electromagnetism, 2nd Ed., McGraw-Hill Book Co., New York (1949), p. 457.