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THE HIGH TEMPERATURE OXIDATION OF ZIRCALOY IN WATER

by

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INFORMATION CATEGORY

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The High Temperature Oxidation of Zircaloy in WaterINTRODUCTION

Although the oxidation kinetics of Zircaloy-2 in water and steam at relatively low temperatures and high pressures are well known, essentially nothing is known about oxidation rates at temperatures and pressures which might be encountered in a reactor in the event of an accident in which coolant pressure and circulation are lost. Under these conditions the temperature of the fuel elements may approach the melting point and the pressure would be near atmospheric. This study was undertaken to provide data which may be used in evaluating the possibility of an explosive reaction of Zircaloy-2 with water under these conditions.

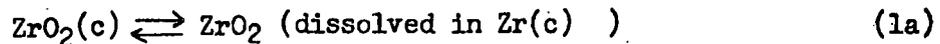
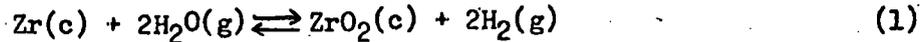
Several studies 1,2,3/ have been made of the extent and violence of chemical reactions in molten metal-water systems and high temperature metal-steam systems. These investigations have indicated that an explosive reaction would not be expected if the metal persists in a massive form or if a layer of steam is present at the metal-water interface. These observations have been verified for the high temperature Zircaloy-2-water reaction.

EXPERIMENTAL PROCEDURE

The materials used were Zircaloy-2 with a nominal composition of 1.5% Sn, 0.12% Fe, 0.10% Cr, 0.05% Ni, balance Zr and Zircaloy-B which is Zircaloy-2 with 5.5% U and 0.037% B added. The samples were ring shaped as shown in Fig. 1, and the effective original surface area was 13 square cm. Details of the sample mounting system are shown in Fig. 2 and the complete system is shown in Fig. 3. High frequency power (450 KC) for heating the sample was supplied by a Westinghouse 10 KW oscillator. The power actually required to heat the samples to their melting point was found to be about 2 KW. Temperature measurements were made with an optical pyrometer sighted on the side of the sample through an opening in the heater coil. These measurements

were corrected by calibration with a standard bulb to allow for intensity losses in the reflecting system and the Vycor tube. The corrected temperatures are believed to be accurate to about $\pm 30^{\circ}\text{C}$.

The reaction at the sample surface is presumed to be



It was assumed that the sample did not absorb an appreciable amount of hydrogen, and also that the effect of the alloying additions upon the stoichiometry of this reaction was negligible. The former assumption is well founded since at the temperatures concerned the solubility of hydrogen in zirconium is negligible. Measurements of the oxidation rate were made by collecting and measuring the volume of hydrogen evolved. This measurement was made by observing the displacement of water from a calibrated volume. The volume of gas was then corrected to standard temperature and pressure. At the lower temperatures and longer times it was found that a cooling jacket above the sample (not shown in Fig. 3) was necessary to prevent excessive water temperatures and consequent steam formation in the column of water above the sample.

For each experiment the sample was placed in position and the entire apparatus filled with water. The sample was then heated rapidly (5-10 sec.) to the desired temperature and maintained at this temperature and the time required to collect successive 250 ml volumes of hydrogen measured. It was found that the sample temperature tended to remain quite constant, requiring only very slight adjustments of the power input over time periods of up to 55 minutes. A steam blanket of the type formed during quenching operations surrounds the sample at the test temperature and heat is transferred from the specimen to the water by convection, conduction, and radiation through the vapor layer. 4/ The apparatus in operation is shown in Fig. 4 with a sample at 1600°C .

EXPERIMENTAL RESULTS

The experimental results are shown in Fig. 5 in which is plotted the logarithm of the weight of metal consumed per unit original area versus log time. The curve shown for 1860°C is based on an observation made when the sample at 1750°C increased in temperature and melted due to a sudden unexpected power surge. The value of this particular curve is doubtful as the surface area of the sample during melting was probably quite different from the original area used in the calculations. The temperature indicated for this sample is also rather questionable and may have been considerably higher. Also shown in Fig. 5 are data for the oxidation of Zircaloy-B at 1600°C. The results are essentially identical to those obtained for Zircaloy-2.

The rate of consumption of metal decreases with time during a short initial period after which it remains constant. The behavior in the initial period is usually associated with the protective action of an adherent oxide scale while the second period is usually considered to begin when the oxide becomes cracked or non-adherent and loses its protective action.

The time to consume all of the metal in an 0.087" thick fuel plate may be calculated from the data of Fig. 5. The results of such a calculation are shown in Fig. 6 as a function of temperature. The reliability of the point at 1860°C is questionable for the reasons indicated previously. Also shown in Fig. 6 are extrapolations from the data of Phalnikar and Baldwin^{5/} for the scaling of unalloyed zirconium in air. Thomas and Chirigos^{6/} have shown that there is a considerable difference between oxidation rates in oxygen and water. They suggest that after "breakaway", which presumably occurs at very short times at these temperatures, an additional factor becomes operative and increases the corrosion rate in water. In view of this and also the possible effect of nitrogen upon the scaling rates for zirconium in oxygen no great significance can be attached to the different slopes observed. Phalnikar and Baldwin^{5/} have found a golden colored phase in the inner oxide film which has been identified as ZrN

by x-ray analysis. This golden phase is replaced by holes as the nitride decomposes. In this work neither holes nor a golden colored phase were found indicating that nitrogen was not present in appreciable quantities and presumably did not contribute to the corrosion.

The appearance of the samples after corrosion is shown in Fig. 7. The amount of metal consumed at 1300°C, 1450°C, and 1600°C was 240, 440, and 540 mg/cm² respectively. The appearance of the external scale is in agreement with the findings of Phalnikar and Baldwin⁵ for zirconium in air in that a black scale appears first and the amount of white scale increases with increasing times and temperature. Sections through the samples are shown in Fig. 8. In this figure it can be seen that the scale thickness is quite uniform indicating uniform heating of the sample surface. Values for the amount of metal consumed calculated from scale thickness are shown in Fig. 5. The agreement with the value calculated from the volume of hydrogen collected is good, verifying the assumptions used in connection with equation (1). The structure near the surface of the sample oxidized at 1450°C is shown in Fig. 9. The other samples have similar structures, differing only with respect to layer thickness. The layers shown in Fig. 9 indicate that oxygen diffuses from the surface into the metal according to equation (1a) resulting in a concentration of oxygen which is high at the surface and decreases toward the center of the sample. The sample may be viewed as a diffusion couple between zirconium and oxygen, resulting in the appearance of the single phase areas of the phase diagram. The expected layers at 1450°C are those indicated in Fig. 9. It is believed that the cracks in the 1600°C sample in Fig. 8 occurred during sectioning. This brittleness is undoubtedly due to a high concentration of oxygen throughout the sample.

During the course of this investigation several samples were heated above the melting point. The appearance of one of these samples is shown in Fig. 10. This sample consisted of a flat disk 3/4" in diameter and 1/2" thick. A carbon sample

holder was used and the entire assembly was placed about 6" under water. This sample was held above the melting point for about 10 seconds. The reaction proceeded quite rapidly but not with great violence, indicating that the oxidation of Zircaloy-2 with water is not self-sustaining for the specimen dimensions employed even at temperatures somewhat above the melting point. Several other samples were melted under water inadvertently, and it was observed that although the reaction proceeded faster, it did not become violent or autocatalytic in nature. It has also been observed during other experiments and also during arc-melting that molten zirconium dropping into water does not react violently. Several explosions have occurred during arc-melting when crucibles burned through, but these have generally been attributed to ignition of the hydrogen produced by the zirconium water reaction.

CONCLUSIONS

1. The oxidation rates of Zircaloy-2 near the melting point in water are approximately those which would be expected from the extrapolation of existing data for the oxidation of zirconium in air.
2. The scales formed during oxidation are essentially the same as those formed during the scaling of zirconium in oxygen, both with respect to appearance and order of formation.
3. Reaction rates are quite fast at the temperatures employed, but are not explosive or excessively violent even at temperatures above the melting point.
4. The presence of small amounts of uranium and boron does not adversely affect the high temperature oxidation rate of Zircaloy-2.

ACKNOWLEDGEMENT

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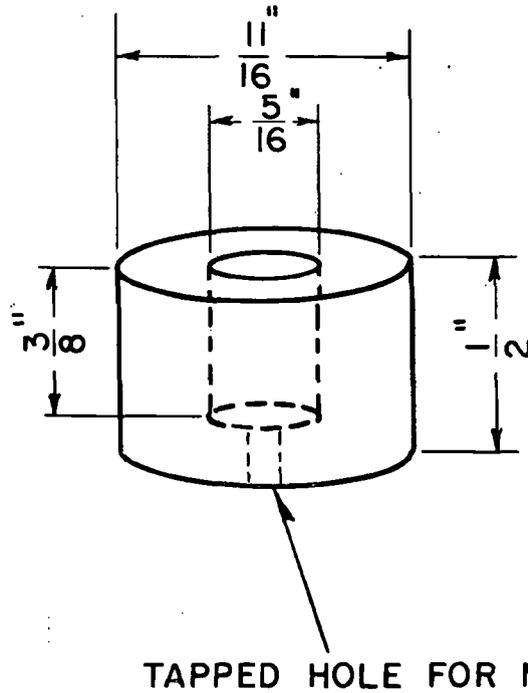


FIG. 1

ZIRCALOY-2 OXIDATION SAMPLE

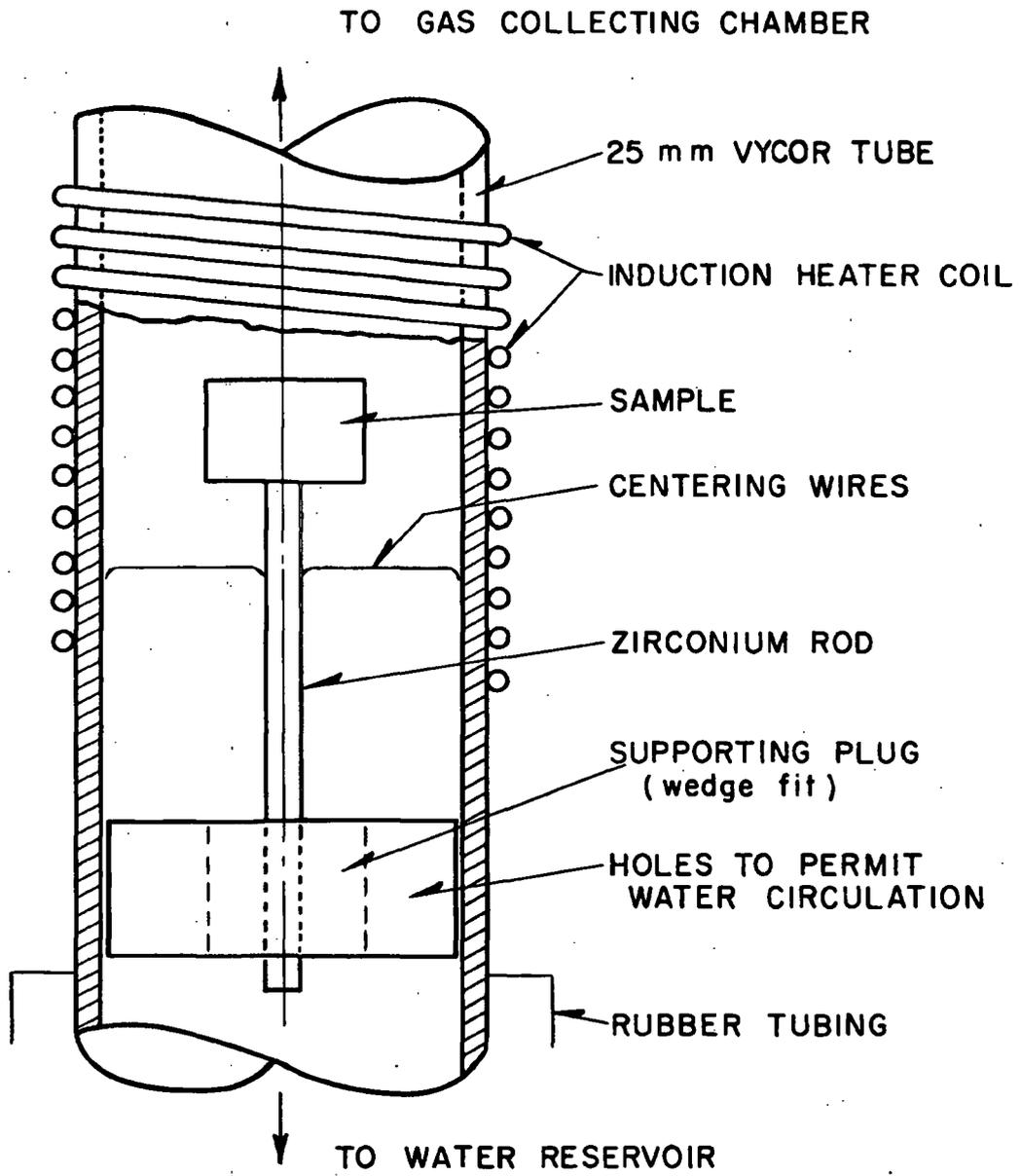


FIG 2
DETAILS OF SAMPLE MOUNTING

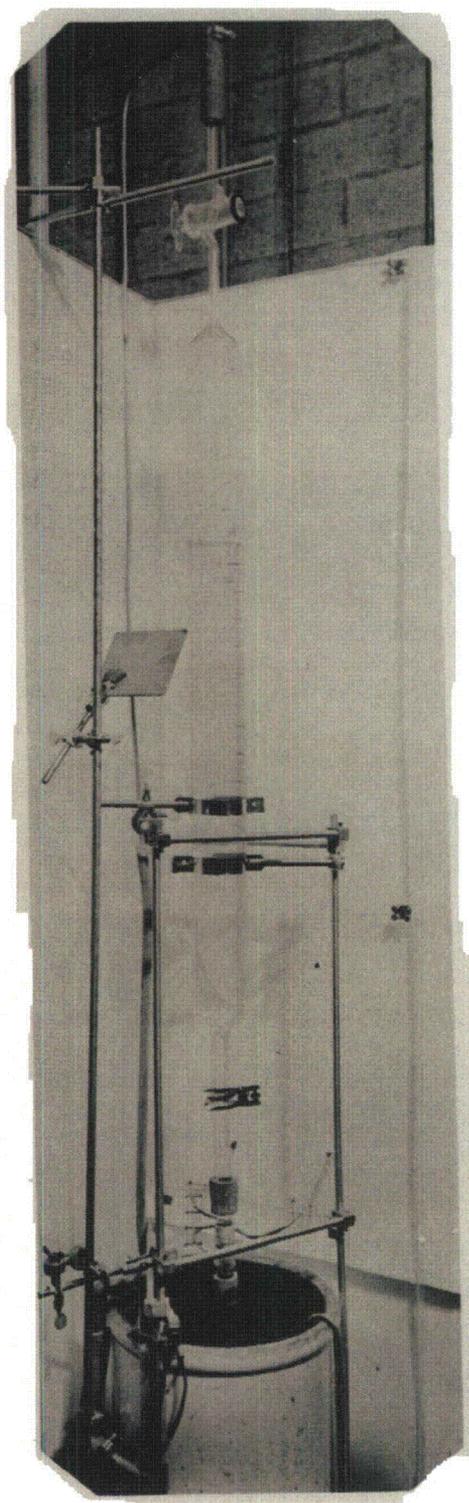


Fig. 3 - High Temperature Oxidation Apparatus

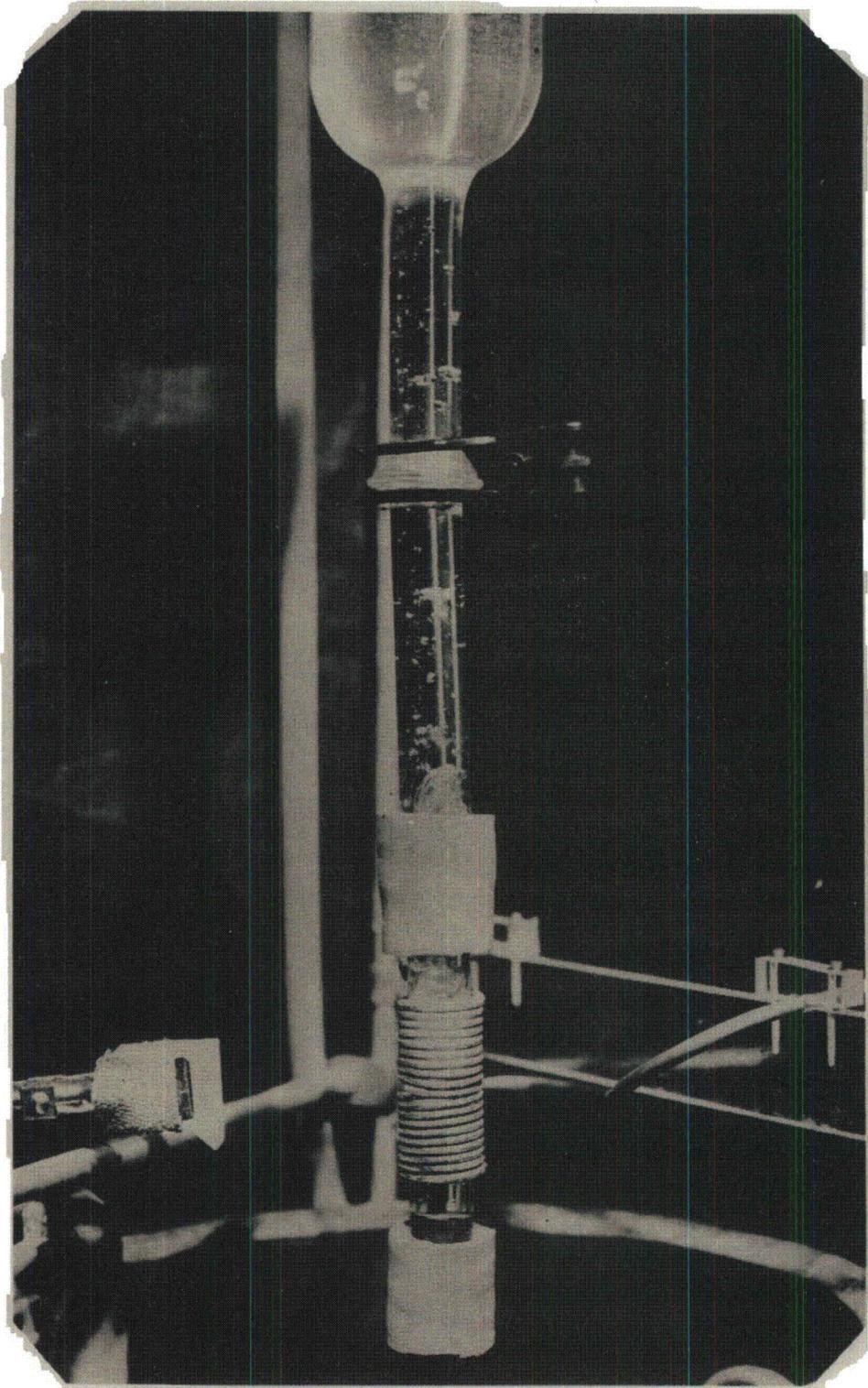


Fig. 4 - Apparatus in Operation with Sample Heated to 1600°C.

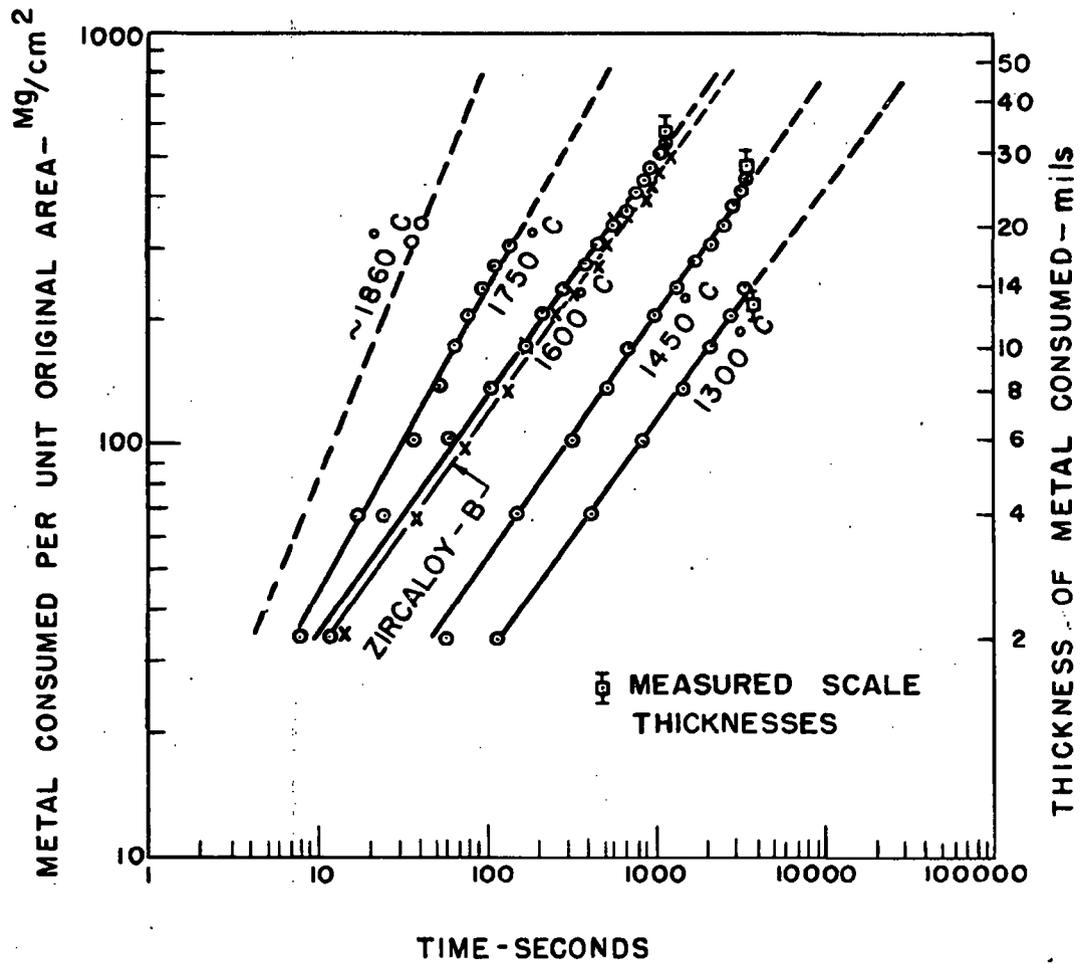


FIG. 5 OXIDATION KINETICS OF ZIRCALOY-2 AT TEMPERATURES ABOVE 1300° CENTIGRADE WHILE SUBMERGED IN WATER

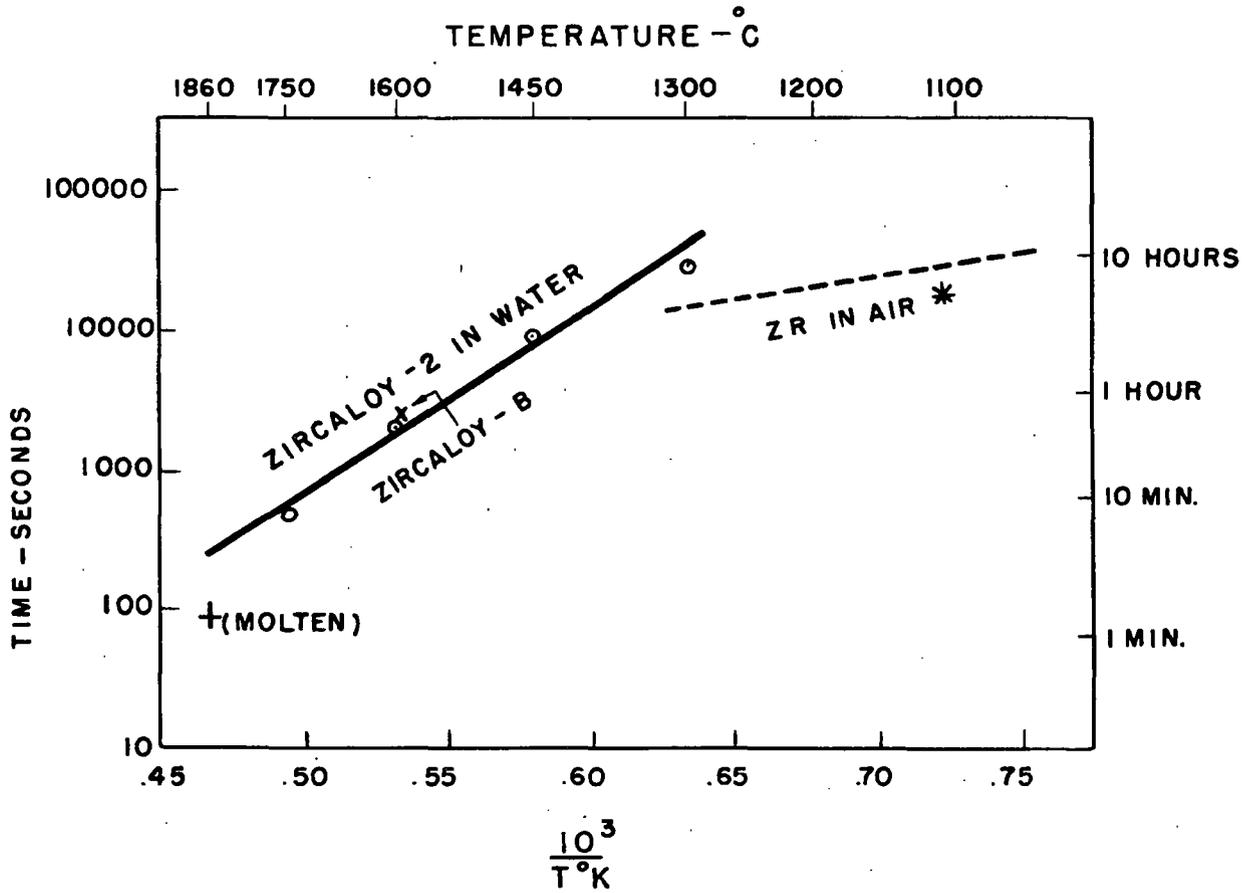
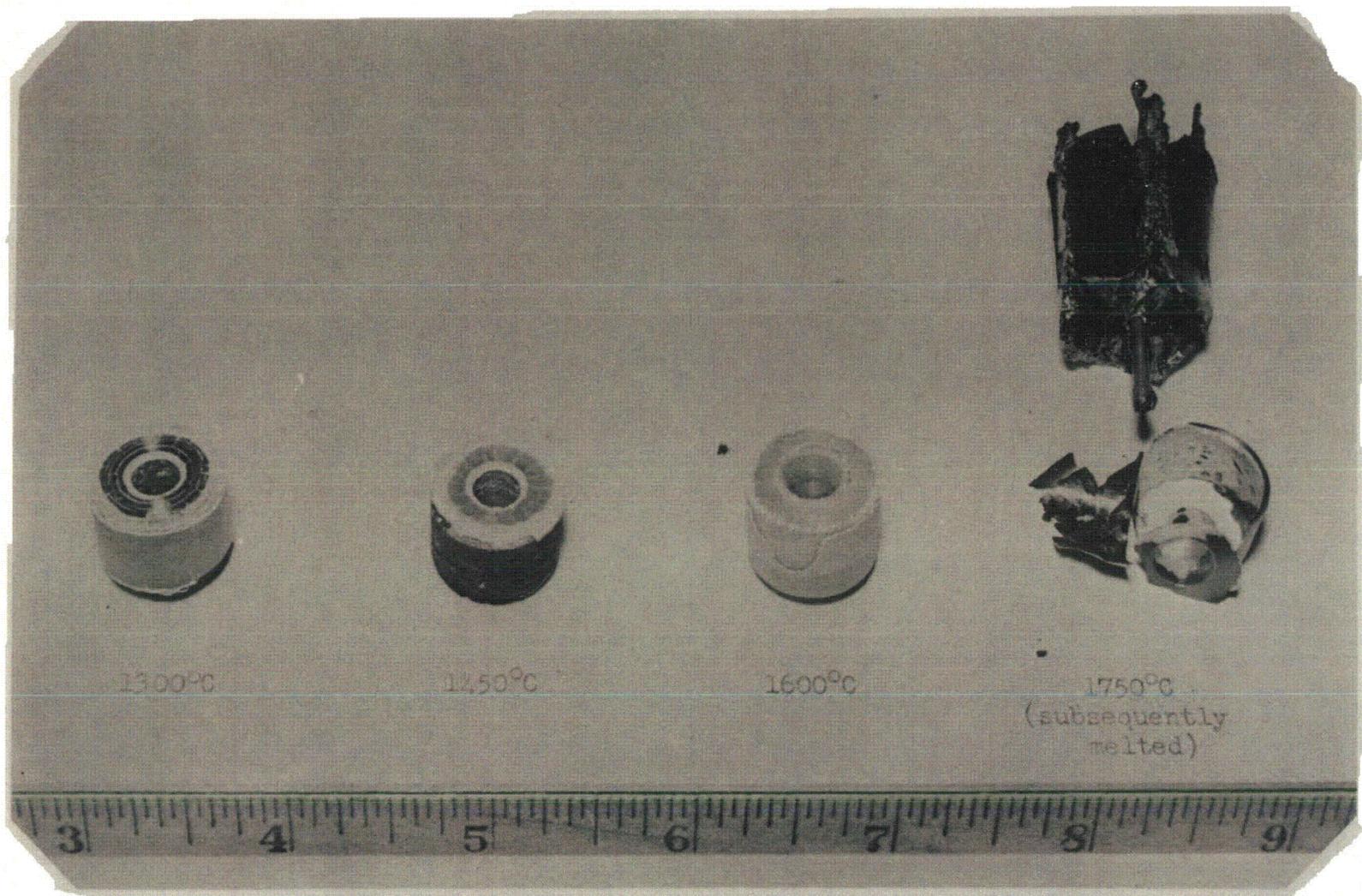


FIG. 6 TIME TO CONSUME 0.087" THICK FUEL PLATE AS A FUNCTION OF TEMPERATURE

* EXTRAPOLATED FROM PHALNIKAR AND BALDWIN¹

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1300°C

1450°C

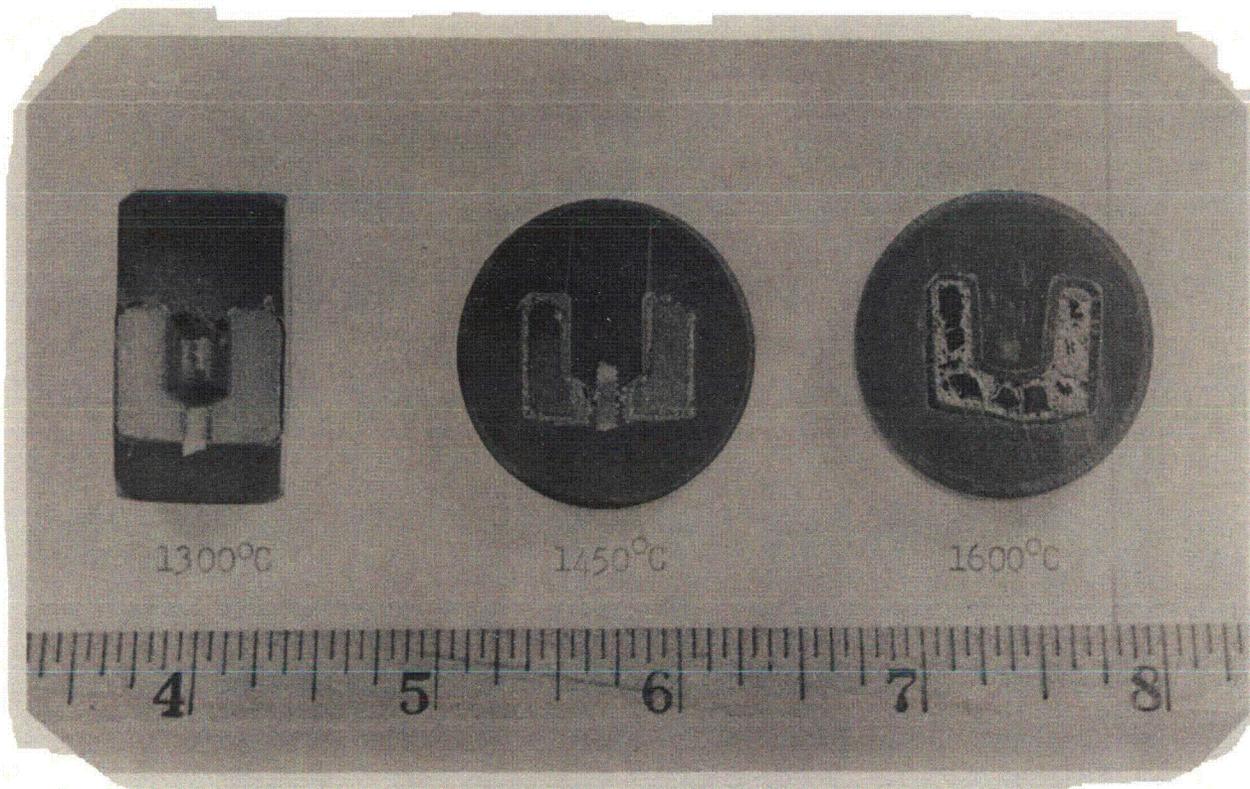
1600°C

1750°C
(subsequently
melted)

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Fig. 7 - Appearance of Zircaloy-2 Samples After Oxidation While Submerged in Water.

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1300°C

1450°C

1600°C

4

5

6

7

8

Fig. 8 - Cross-section of samples shown in Fig. 7

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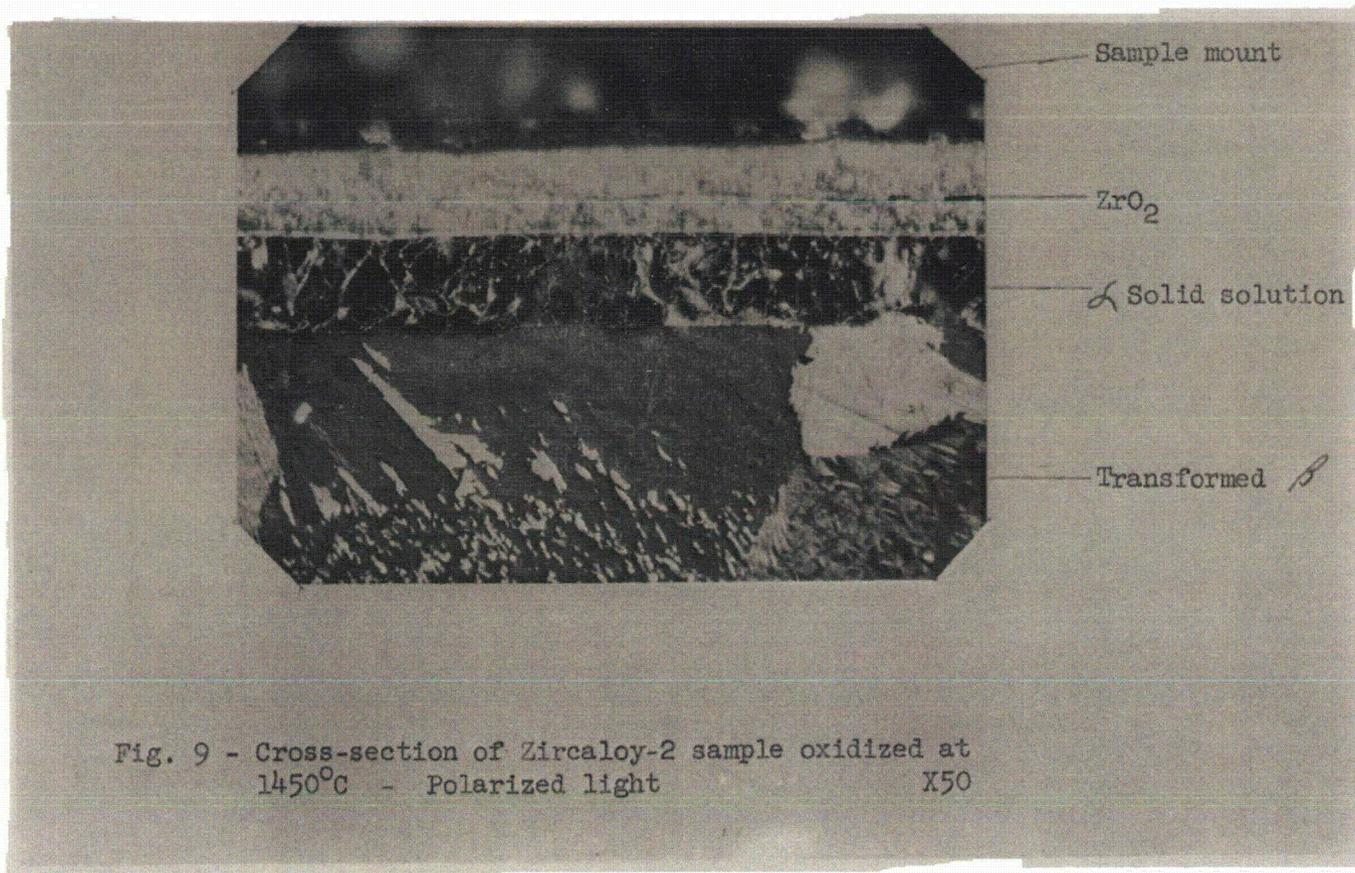


Fig. 9 - Cross-section of Zircaloy-2 sample oxidized at
1450°C - Polarized light X50



Fig. 10 - Appearance of Zircaloy-2 Sample Held 10 Sec. Above the Melting Point While Submerged in Water.