MASTER

**RECOMMENDED PROPERTY AND REACTION KINETICS
DATA FOR USE IN EVALUATING A LIGHT-WATER-COOLED REACTOR
LOSS-OF-COOLANT INCIDENT INVOLVING
ZIRCALOY-4 OR 304-SS-CLAD UO₂**

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ABSTRACT

Selected values are presented for the high temperature physical and mechanical properties of fuel element materials involved in a loss-of-coolant incident in a boiling water or pressurized water nuclear reactor. The fuel element materials considered are Zircaloy-2 and -4, 304 SS, and UO_2 . Where possible, the property values have been critically evaluated taking into consideration the meltdown environment of steam or steam and air.

The physical properties discussed are: melting point, boiling point, heat of fusion, heat of vaporization, vapor pressure, phase transformations, coefficient of thermal expansion, density, total normal emittance, thermal conductivity and enthalpy and heat capacity. The mechanical properties discussed are: tensile strength, ductility, compressive strength, and modulus of elasticity. In most instances, values of various properties are given as a function of temperature to the melting point of the material.

The kinetics of the oxidation reactions of the cladding materials with steam are also discussed and equations presented for calculation of oxidation rates under isothermal conditions for one atmosphere of steam.

I. INTRODUCTION

The purpose of this report is threefold: (1) to summarize the available pertinent information on physical and mechanical properties of fuel element materials involved in a loss-of-coolant incident in a boiling water or pressurized water nuclear reactor, (2) to discuss the known high-temperature physical and chemical behavior of the component materials so that the behavior of the composite system under loss-of-coolant conditions may be postulated insofar as existing data permit, and (3) to delineate particular values for the various physical, mechanical, and chemical properties for use in hazard model calculations taking into account the potential chemical and physical environment which could affect these properties. The specific materials of concern are UO_2 fuel, and Zircaloy-4^{*} or 304L stainless steel^{**} cladding. The scope of this report, however, is limited to a temperature excursion to the point of melting the core constituents; the behavior of these molten materials after they leave the original core position is not covered.

Assumptions for this study are that the reactor core is water cooled under about 2000 psi pressure, the fuel element maximum cladding temperature during operation is about 350°C , the internal temperature of the UO_2 is as high as 2300°C (for 1.25-cm-dia. UO_2 fuel rods), and a rupture occurs which results in loss of coolant from the reactor core. Subsequently,

* The composition of Zircaloy-4 is 0.005-0.15% Cr, 0.18-0.24% Fe, 1.2-1.7% Sn, remainder Zr.

** The composition of 304L stainless steel is < 0.03% C, < 2% Mn, < 1% Si, 18-20% Cr, 8-12% Ni, remainder Fe.

the reactor core temperature rises because of nuclear afterheat even though the fission reaction has been stopped by the insertion of the control rods or loss of moderator.

While there will be extremely variable conditions in the core during meltdown following a loss-of-coolant incident, knowledge of the properties of the fuel element materials and their oxides at high temperatures can contribute greatly to an understanding of the mechanisms involved and enhance the accuracy of pre-analyses of such incidents. Empirical data on the effects of melting also can contribute to this better understanding.

The discussion and data in this report are presented under the following headings:

- II - Significant Loss-of-Coolant Incident Variables
- III - High Temperature Physical and Mechanical Properties of the Fuel - Core Materials
- IV - Reaction Kinetics of Fuel-Core Materials
- V - General Consideration of Irradiation Effects and Uranium Burnup

II. SIGNIFICANT LOSS-OF-COOLANT INCIDENT VARIABLES

There are many inter-related variables which affect the behavior of core materials after loss of coolant. Some of the more pertinent and significant ones that may affect materials properties are discussed in this section.

RATE OF TEMPERATURE INCREASE

After a reactor scram because of loss of coolant, the rate of temperature increase in the core is dependent upon the release rate of delayed nuclear heat, the generation rate of heat by reaction of the core materials with steam and/or air, the release rate of heat to the surrounding environment, and the heat capacity of the core. A heating rate range of 0.3° to 10°C per second was selected as representative of a loss-of-coolant incident and it was assumed that the core temperature will continue to rise until it exceeds the melting point of UO_2 (i.e., above $\sim 2840^{\circ}\text{C}$). To predict the probable rate at which the core temperature will increase requires knowledge of the amount of U burnup prior to the loss-of-coolant incident, and knowledge of the high-temperature properties of the materials and their potential chemical reactions and interactions with the environment at temperatures to the melting point of UO_2 . For example, both the thermal conductivity and melting point of UO_2 are reduced by fissioning of the uranium. While a certain measure of recovery in the thermal conductivity is to be expected as the temperature increases, the probable overall effect of U burnup is a reduction of the time to melting and a lowering of the temperature required for melting.

CORE ATMOSPHERE

When the coolant is lost, some water is assumed to remain in the bottom of the pressure vessel and some air may flow into the vessel. As the core temperature increases in the presence of water and/or air, the metal (M) cladding will begin to oxidize according to the reactions:

and

UO₂ will oxidize initially according to the reactions:

and

ΔH being the heat evolved in the reactions. The considerable quantities of heat released accelerate the overall rate of temperature increase in the core. Lustman⁽¹⁾ and Epstein⁽²⁾ showed the magnitude of the thermal effect for oxidation of Zircaloy-clad UO₂ fuel. As steam is generated, it will tend to flow upward through the core, reacting with hot core materials to form the metal oxides and hydrogen; the hydrogen-steam mixture will be less oxidizing than the steam alone, and may result in lower oxidation rates in the upper part of the core. Therefore, the environment to which the clad UO₂ fuel pins will be exposed will be an oxidizing atmosphere with a large variation in oxidizing potential during the thermal excursion. This atmosphere will exist until the available

water and air are exhausted of oxygen or, if sufficient oxygen is available, until the core materials are completely oxidized. In other words, the atmosphere to which the fuel is exposed may or may not have an oxidizing potential as the core materials melt.

CORE GEOMETRY ALTERATIONS

If the rate of temperature increase is relatively low and if sufficient oxygen is present as water and/or air, the oxide film formed and the cladding may cause alterations in the core geometry as the metal cladding melts. For example, it has been observed that stainless steel, after appreciable oxidation^(3,4), shows a "frothing" effect when melted. This effect may alter the behavior during core meltdown by blocking coolant passages, thereby accelerating the rate of temperature increase and causing more rapid melting of the core material in the upper part of the core; and it may also promote more cladding reaction with UO_2 to form lower melting compositions. Thus, the cladding may reach its melting point with varying degrees of oxidation depending on the heating rate and the amount of oxygen available.

If the heating rate is very rapid (i.e., $> 3^\circ\text{C}$ per second), an appreciable quantity of unoxidized metal cladding may melt and flow toward the bottom of the core and containment vessel. For Zircaloy cladding, the flow of molten metal toward the bottom may be influenced by reaction with the UO_2 , forming U metal, ZrO_{2-x} , and ZrO_2 . The extent of these reactions will, of course, depend on the length of time the molten cladding is in contact with the UO_2 , the amount of oxidation of the cladding, and the extent to which flow is impeded by blocked passages, etc.

III. HIGH-TEMPERATURE PHYSICAL AND MECHANICAL PROPERTIES OF THE FUEL CORE-MATERIALS

As previously discussed, reactions of fuel element materials during the thermal excursion of the core will result in compositional changes and properties different from those of the original materials. The Zircaloy cladding of the UO_2 will oxidize, forming a double layer of oxide⁽³⁾ (ZrO_2 and ZrO_{2-x}) and metal phase with an oxygen content of up to 29.7 atomic percent^(5,6). Thus, the properties of the Zircaloy metal, the ZrO_2 outer layer on the Zircaloy, and the UO_2 are of predominant importance. The stainless steel will also oxidize, but it may behave differently from Zircaloy, e.g., it may form a thinner oxide film, and the constituents of the stainless steel do not absorb large amounts of oxygen. Thus, for fuel elements clad with stainless steel, the materials of most significance are the stainless steel metal and the UO_2 . Based on these considerations, property data are included for ZrO_2 as well as for Zr, Zircaloy, Type 304 SS, and UO_2 . The data on Zr are included since, in some instances, the data for Zircaloy are not available and the property data on zirconium are suggested for use where the difference in composition between the metal and alloy should cause no significant change in the property.

Because of the considerable spread in values that has been reported for certain property data for a given material, a critical evaluation was performed in order to recommend, where possible, a "best set" of values for the particular property concerned. In addition, where the properties may

be affected by exposure to the probable chemical and physical environment, the influence of the environment is discussed and pertinent data presented where available. For some properties, insufficient data exist to allow a selection of the most probable value; in these instances, the effects of composition and/or other pertinent factors on the property are discussed in an attempt to point out the most probable value. The critical physical property data for these materials (for temperatures generally above 1000°C) are given in Table I, and mechanical property data are given in Table II.

A. PHYSICAL PROPERTIES

The available physical property data recommended for use in studies related to reactor core meltdown in steam and/or air, for a core containing UO_2 fuel pins clad with either Zr alloy or 304 SS, are given in Table I. Where data are not complete up to the melting point, additional studies to complete the information are either under way or planned. The data of Table I are discussed below.

1. Melting Points

Zircaloy-4 and Reaction Products - The reported melting point of Zircaloy-4 is about the same as that for unalloyed Zr⁽⁷⁾; the relatively small amount of alloying agents, about 2 weight percent, does not result in a significant change in the melting behavior. Dissolved oxygen will raise the liquidus to a maximum of $\sim 1975^{\circ}\text{C}$ ^(5,6). The melting point of ZrO_2 is $\sim 2700^{\circ}\text{C}$ and the ZrO_2 - UO_2 eutectic is $\sim 2650^{\circ}\text{C}$ ^(8,9). The melting point of UO_{2+x} - ZrO_2

mixtures is probably considerably lower than that of $\text{UO}_{2.00} - \text{ZrO}_2$. Parker⁽¹⁰⁾ reports that a ZrO_2 -Zr- UO_2 sample prepared by melting a Zircaloy-clad UO_2 fuel specimen in air was found later to melt at 2150°C in air and 2450°C in vacuum. The melting point of a similar mixture in steam would probably be intermediate in temperature.

304 SS - The melting point of 304 SS is not a fixed value since this Fe-base alloy contains relatively large quantities of Cr and Ni and, therefore, melts with a liquid and solid present simultaneously over a temperature range of about 55°C . A melting point of 1400°C is recommended.

UO_2 -SS Oxides - Parker⁽¹⁰⁾ measured melting points of UO_2 -oxidized-SS compositions in air and steam. The compositions approximated those expected if one-fourth, one-half, and all of the stainless steel in a reactor core were homogeneously mixed with the UO_2 fuel. Melting points were determined in both air and vacuum. Melting points in air ranged from 1435°C with the highest amount of SS oxide to 1650°C for the one-fourth case; in vacuum, the corresponding melting points ranged from 1750° to 2600°C .

UO_2 - The melting point of UO_2 has been measured by many investigators with varying results; even the most recent measurements are not in complete agreement. They range from $\sim 2800^\circ\text{C}$ to $\sim 2880^\circ\text{C}$ ^(11,12). The data of Latta and of Bates are shown in Figure 1. Both curves show the likelihood of a maximum melting point near the stoichiometric point, but the exact composition for such a maximum has not been determined. Individual measurements in

the range $\text{UO}_{2.000}$ to $\text{UO}_{2.003}$ by both investigators indicate the possibility of a decrease in melting point with increasing O/U in this range. Latta's work was performed in a closed system which tended to prevent any change in UO_2 stoichiometry, and in addition the O/U ratio was determined after the melting point determinations were made. For these reasons, the data of Latta are selected as being more reliable for the melting point of UO_2 .

Data describing the effect of U burnup on the melting point of UO_2 are limited and in definite disagreement. Work at Hanford⁽¹³⁾ showed an increase of $\sim 130^\circ\text{C}$ (from 2800° to 2930°C) for low burnups (400 to 1000 MWD/MTU) and a melting point of $\sim 2800^\circ\text{C}$ (same as obtained by Hanford for unirradiated UO_2) for burnups between 3500 and 50,000 MWD/MTU. Work at Westinghouse (WAPD)⁽¹⁴⁾ showed a decrease of $\sim 30^\circ\text{C}$ per 10,000 MWD/MTU. Their lowest burnup sample was 2000 MWD/MTU, which is above the burnup level for which Hanford showed the peak in melting temperature.

In summary, the "true" melting point of unirradiated $\text{UO}_{2.000}$ is in the range of 2800° to 2880°C . Considering the effects of additional oxygen and burnups of less than 10,000 MWD/MTU, a "best" value for the melting point of UO_2 for use in loss of coolant analysis is 2840°C .

As can be deduced from the above discussion of melting points for the initial materials involved, and considering the multitude of compositions that are possible during various stages of the thermal excursion, it is impossible to accurately define the overall melting behavior of the core

under loss-of-coolant conditions. However, in the case of Zircaloy-clad UO_2 , it appears that the lowest temperature for molten material to be present is 1850°C (m.p. of Zircaloy-4), or possibly 1975°C , the m.p. for oxygen-saturated Zr. In the case of stainless steel, the minimum temperature is 1400°C or essentially the solidus boundary of the Fe-Cr-Ni system at the 304 SS composition.

While a certain amount of melting may occur in the Zircaloy-4- and 304 SS-clad systems at the above mentioned temperatures, it should be noted that the fluidities of the various melts are unknown. In general, while the viscosity of the metal and oxide liquids will be low (i.e., below about 10 centipoises), the melt composite material (i.e., a mixture of molten metal and solid oxide) may be sufficiently viscous not to flow initially. If sufficient steam is available, this viscous character of the "melt" will persist to temperatures much higher than those listed for minimum liquid formation.

It should also be noted that the 304 SS-clad control rod, used in some reactor designs, may react with the Zircaloy-4 and produce a liquid at a temperature as low as 935°C , the eutectic between Fe and Zr⁽¹⁵⁾.

2. Boiling Points

Zircaloy-4 - The boiling point of Zircaloy-4 is considered to be essentially the same as that for Zr, although it must be recognized that the small quantity of Sn in this alloy can initiate boiling at a somewhat lower temperature. (Sn has a boiling point of about 2720°C .)

304 SS - The boiling point of 304 SS is considered undefined because of the alloying. The values for the three major constituents of this alloy, listed in Table I, are seen to be below the melting point of UO_2 .

3. Heat of Fusion

Zircaloy-4 and 304 SS - The heat of fusion of Zircaloy-4 probably differs little from that of Zr. On the other hand, that of 304 SS probably depends on those of its principal constituents, which are listed in Table I.

UO_2 - The only calorimetrically determined value for the heat of fusion of UO_2 is 18.2 ± 0.5 kcal/mole reported by GE-NMPO⁽¹⁶⁾ and shown in Figure 2. Grossman⁽¹⁷⁾ reported a value of 25.3 ± 4.0 kcal/mole based on thermal arrest data from a tungsten capsule containing UO_2 cooling in a vacuum. This is a refinement of his earlier value of 28.5 ± 7.5 kcal/mole⁽¹⁸⁾. These values may be compared with a theoretical value of 21.2 kcal/mole derived by Epstein⁽¹⁹⁾ based on application of ideal solution theory to the UO_2 - PuO_2 phase diagram, and with a value of 18.6 kcal/mole obtained as the approximation $3 RT_m$. The value of 18.2 kcal/mole is recommended.

4. Heat of Vaporization

Zircaloy-4 - The heat of vaporization of Zircaloy-4 is considered to be the same as that for unalloyed Zr.

304 SS - The data for 304 SS are the values for the elements present in this alloy.

5. Vapor Pressure

Zircaloy-4 - The vapor pressure of Zircaloy-4 is expected to be somewhat higher than that of unalloyed Zr because of the relatively low boiling point of Sn (2720°C).

UO₂ - The vapor pressure of UO₂ is reported as the total pressure including UO₂ and UO₃ in the vapor phase. At O/U ratios higher than 2, which would be expected in a loss-of-coolant incident, the UO₃ and the total pressure would be greater than for stoichiometric UO₂. For example, Alexander et. al.⁽²⁰⁾ show that the total pressure over UO_{2.03} is about 2.2 times that over UO_{2.00} in the temperature range 1700° - 2500°C. Calculated equilibrium composition values for UO_{2+x} in steam are UO_{2.16} at 1800°C and UO_{2.13} at 2200°C. The vapor pressures of these compositions are expected to be greater than those of UO_{2.03}.

ZrO₂ - The reported vapor pressure of ZrO₂⁽²⁰⁾ is believed accurate, but in the presence of metallic Zr, gaseous ZrO is formed with a considerably higher vapor pressure than that of either the metal or ZrO₂. The pressure of ZrO can be approximated in atmospheres by

$$\log P = -34,383/T - 7.98 \times 10^{-4}T + 14.89^{(21)},$$

where $T = ^\circ K$.

In the steam atmosphere of the loss-of-coolant incident, it is very unlikely that the vapor pressure of ZrO need be considered.

6. Phase Transformations

Zr and ZrO₂ - Zirconium exists in the hexagonal α form below 862°C and, in the absence of dissolved oxygen, in the body-centered-cubic β phase above this temperature⁽¹⁵⁾. The temperature of transformation increases with increasing oxygen content as shown in Figure 3. The heat of the α - β transformation in Zircaloy-2 is 970 cal/g-atom⁽²²⁾.

Zirconia exists in three forms, monoclinic below 1100°C, which transforms between 1100°C and 1250°C to a tetragonal phase, and a cubic phase stable above 2285°C⁽⁹⁾. Gebhardt et. al.⁽⁶⁾ report the cubic phase may exist at temperatures as low as 1600°C. Ruh and Garrett⁽²³⁾ found the cubic phase in ZrO_{1.7} above 1490°C, as shown in Figure 4. The transformation from monoclinic to tetragonal is accompanied by linear shrinkage of the order of 1%⁽⁸⁴⁾.

UO₂ - No transformations occur in stoichiometric or nonstoichiometric urania at high temperatures over a wide range of compositions.

7. Coefficient of Thermal Expansion

Zircaloy-4 - An equation for the instantaneous coefficient of linear thermal expansion of Zircaloy-2 is given in Table I for the α -phase range only⁽²⁴⁾. Expansion above the transition temperature is probably similar to that of β Zr, which is also given in Table I.

304 SS - The mean coefficient from 0° to 1000°C for 304 SS is shown in Table I⁽²⁵⁾.

UO₂ - The best data for the linear thermal expansion of UO₂ appear to be those of Conway⁽²⁶⁾ based on experiments conducted between 1000° and 2250°C (see Figure 5). For higher temperatures, Christensen⁽²⁷⁾ has published results to near the melting point which straddle an extrapolation of Conway's curve. Christensen's coefficient of linear expansion for molten UO₂ is $3.5 \times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$ from the melting point to $\sim 3200^{\circ}\text{C}$.

Conway's equation, as listed in Table I, is recommended for extrapolation in the temperature range from 2250°C to the melting point.

ZrO₂ - Linear thermal expansion of monoclinic ZrO₂ was calculated from the data of Grain and Campbell⁽⁸⁴⁾ and is shown in Figure 6.

8. Density

Room-temperature density values are listed in Table I, and the density changes with temperature may be computed from the linear expansion data in the table. The density of UO₂ at its melting point and above is of special interest. Christensen's⁽²⁷⁾ values were 9.7 g/cc for the solid at $\sim 2800^{\circ}\text{C}$ and 8.8 g/cc for the liquid, from which he concluded there is a density decrease of 9.6% upon melting. Christensen's values of the absolute densities at 2800°C (solid) and $> 2800^{\circ}\text{C}$ (liquid) may not be precise but the 9.6% change upon melting is considered a precise value.

9. Total Normal Emittance

Emittance is a highly variable property because of its great dependence on the roughness and reflective properties of the surface. The total

normal emittance of metals depends upon the degree of oxidation of the surface and the opacity of the oxide layer formed; the opacity of the oxide layer may, in turn, be dependent upon its thickness and density.

Cox⁽²⁸⁾ gives an excellent summary of various factors affecting emittance values for various classes of materials. This summary also considers some of the precautions to be observed when an emittance value determined under one set of conditions is used for calculations involving greatly different conditions.

The total normal emittance values for Zr and 304 SS are presented in Table I.

Zircaloy-2 - Total hemispherical emittance values for Zircaloy-2 with up to 22 atomic percent oxygen in solution have been measured by Lemmon⁽²⁹⁾ over the temperature range of $\sim 800^{\circ}$ to 1800°C . The values increased slightly with temperature, and for a high-oxygen-content sample were ~ 1.5 times those of a low-oxygen sample. The values for the low-oxygen content were ~ 0.2 to ~ 0.26 and for the high-oxygen content, ~ 0.315 to ~ 0.33 in this temperature range. While these data are applicable to Zircaloy and to Zircaloy with a high oxygen content, they are not considered representative of Zircaloy in a reactor undergoing continuous oxidation in steam. This is principally because of the presence of a film of oxide on the surface of the metal which materially affects emittance. Initially, this film may be considered to be $\sim 0.1 \mu$ thick, either because of prior autoclave treatment or from the oxidation in the reactor during startup.

In the work reported by Lemmon⁽²⁹⁾, oxygen was introduced into the Zircaloy-2 by adding small volumes of oxygen to the system and equilibrating the gas with the sample. Emittance was then measured at a given temperature. Measurements made immediately after the incremental oxygen addition (Curve A Figure 7) were much higher than those of the equilibrated sample (Curve B Figure 7). This indicates that initially-formed oxide film substantially increased the emittance. In one test run at $\sim 825^{\circ}\text{C}$, the final oxide film thickness was approximately $10\ \mu$ and the final total emittance was ~ 0.7 . The data indicate that emittance was still increasing with each oxygen addition. If it is assumed that the oxide film thickness increased linearly with each oxygen addition, then correcting for the effects of oxygen diffusion into the metal during cooling to room temperature and reheating after half the oxygen was added, an estimate may be made of emittance as a function of oxide thickness. The following values are derived using the above assumption and a value of 0.22 for unoxidized Zircaloy:

Oxide Film Thickness, microns	Total Emittance at $\sim 825^{\circ}\text{C}$
0	0.22
0.5	.32
1.25	.38
2.5	.50
5.0	.62
7.5	.67
10	.70

For these emittance values to be of use in the loss-of-coolant case, probable oxide thicknesses must be determined as a function of temperature-rise rates. If the reactor is assumed to have operated 500 days at 300°C before the loss of coolant, the equation of Whitmarsh⁽⁷⁾ would predict the formation of 1 additional micron of oxide. Additional oxide thickness expected during the thermal surge for temperature-rise rates of 0.3° and 3°C/sec were interpolated from oxide thickness measurements on Zircaloy samples heated at these rates to various temperatures⁽³⁰⁾, and were estimated for a rate of 10°C/sec. Total expected oxide thicknesses are tabulated below for the cases of loss of coolant immediately after startup and after 500 days operation. It is possible that the corrosion rate in reactor is faster than indicated in ORNL-3281⁽⁷⁾. A later revision of this work is in ORNL-3476⁽⁷⁾ which indicates that the corrosion rate on exposure to fast neutrons is probably 2 to 3 times the unirradiated rate. In this case, the figures above for 500 days would apply to about 200 days reactor operation.

Temperature Rise Rate, °C/sec	Oxide Film Thickness (microns) vs Maximum Temperature			
	500°C	800°C	1000°C	1200°C
0.3	0.1 to 1	0.5 to 1.5	5.6 to 6.6	~ 40
3	0.1 to 1	0.2 to 1.2	1.2 to 2.2	~ 9
10	0.1 to 1	0.1 to 1.1	0.6 to 1.6	4-5

Based on the above discussion and assuming that steam is always available to oxidize Zircaloy, the following emittance values for Zircaloy-4 are recommended for use under loss-of-coolant conditions:

Temperature Rise Rate, °C/sec	Emittance vs Clad Temperature		
	800°C	1000°C	1200°C
0.3	0.32 to 0.40	0.63 to 0.65	0.72
3	0.26 to 0.38	0.38 to 0.46	0.69
10	0.24 to 0.36	0.33 to 0.43	0.52 to 0.62

It might be expected that the emittance of Zircaloy with an oxide coating would approach that of bulk ZrO_2 as the oxide thickness increases. However, the data of Lemmon show emittance rising from 0.22 for the unoxidized alloy to 0.7 for a 10 μ oxide film, considerably above the value of ~ 0.34 shown in Figure 8 for calcia-stabilized bulk ZrO_2 at 825°C.

This discrepancy could be the result of (1) impurities (NiO , FeO) in the oxide film, (2) non-stoichiometry of the oxide, (3) transparency of the oxide, (4) crystallographic structure of the oxide, (5) presence of stabilizing agent (CaO), or (6) temperature measurement errors. At the Southern Research Institute⁽³¹⁾, the total normal emittance of calcia-stabilized ZrO_2 was less than 0.4 at 1425°C in the presence of air, compared to 0.8 in an inert atmosphere. The difference was attributed to either impurities or differences in stoichiometry. Clark and Moore⁽³²⁾ found that the spectral emittance of sintered calcia-stabilized ZrO_2 changed with time for incompletely stabilized material, increasing at short wavelengths and decreasing progressively at longer wavelengths. The fraction of monoclinic ZrO_2 in this material was found to have increased

by a factor of three after heating for 5 hours at about 1330°C . Considering the information available for the oxidized Zircaloy and for the bulk CaO-stabilized ZrO_2 , the possibility exists that the emittance of Zircaloy may reach a maximum value for the continuously steam-oxidized material and then decrease as the oxide film becomes thicker.

304 SS - Very thin oxide films on stainless steels cause very large changes in emittance. Oxidation of an 18-8 SS at low temperatures ($\sim 500^{\circ}\text{C}$) results in variations by as much as a factor of ~ 5 (0.15 to 0.85) in emittance. The equation for an oxidized 18-8 SS given in Table I is derived from the data of Sully, et. al.⁽³³⁾, and is believed to be adequate for 304 stainless steel.

UO_2 - Total emittance data for UO_2 are not available, but Held⁽³⁴⁾ has measured spectral hemispherical emittance of UO_2 and found values near 0.8 (i.e., 0.70 to 0.88) for UO_2 at 0.656 and 0.70 μ . His values increased slightly with increasing O/U ratio and with increasing wavelength.

ZrO_2 - The data for ZrO_2 ($\text{ZrO}_2 + 22 \text{ wt. } \% \text{ CaO}$) reported by Cox⁽²⁸⁾ are presented in Figure 8, which also shows the data of Hedge⁽³⁵⁾.

10. Thermal Conductivity

Variations over a decade or two in thermal conductivity values reported for nominally the same material are not uncommon. Some of this variation is undoubtedly because of poor measurement technique; however, in some

materials small differences in chemical composition and microstructure can result in large changes in thermal conductivity. The particular effect may also be temperature dependent, that is, the effect may be large at low temperatures and become unimportant at elevated temperatures. For example, the effect of porosity can be very significant at low temperatures; but at high temperatures ($> 1800^{\circ}\text{C}$), be greatly decreased. In the loss-of-coolant environment the presence and arrangement of the metal and oxide phases in the clad material can have a major effect on the thermal conductivity of the composite.

The above brief discussion is not intended to detail all the factors affecting thermal conductivity, but to indicate that when using thermal conductivity values for a material involved in heat flow or thermal gradient calculations, it cannot always be assumed that the data being used apply to a given material just because the "name" is the same.

Zircaloy-4 - The thermal conductivity of Zircaloy-4 has been reported by Feith⁽³⁶⁾ from about 400° to 1500°C , by Scott⁽³⁷⁾ from 80° to 780°C , and by Chirigos, et. al.⁽³⁸⁾ from 100° to 850°C . The data are presented in Figure 9. Scott's data were obtained on tubing and the maximum scatter of his data about a least-squares-computed line was $\pm 10\%$. The average values from Feith are within $\pm 5\%$ of the smoothed curve. Feith's data show a distinct increase in dk/dT above about 1000°C .

Chirigos reported data for both Zircaloy-2 and -4. The data for Zircaloy-4 are in excellent agreement with Feith's values from 100° to 600°C . Above

600°C, Chirigos' data indicate a marked increase in conductivity with temperature and at 850°C are ~ 13% greater than Feith's. On the other hand, the Zircaloy-2 data are in excellent agreement with Feith's data to 850°C. The precision of the data reported by Chirigos is not known.

Chirigos referenced his data source as a "Private Communication from J. Matolich, BMI, Columbus, Ohio", and a literature search did not reveal that the details and results of Matolich's work were published elsewhere.

Feith's data are recommended for use in loss-of-coolant calculations. However, as cautioned previously in discussing factors affecting thermal conductivity, the errors involved in applying the thermal conductivity of Zircaloy-4 per se to Zircaloy-4 with a variable oxide thickness and high oxygen content metallic layer underneath the oxide layer should be considered carefully. The latter is the material which is expected in the loss-of-coolant case. That this consideration can be important is illustrated by the following. An estimate of the effect of the oxide layer on the Zircaloy-4 at 1200°C was made, assuming that (1) the Zircaloy-4 clad is 0.051 cm in thickness, (2) a 0.0051 cm thickness of ZrO_2 has formed with a conductivity of 0.0256 W/cm-°C, and (3) the conductivity of the oxygen-rich material and Zircaloy-4 both are 0.31 W/cm-°C. The results indicate that the thermal conductivity in the radial direction (tube thickness) will be reduced from 0.31 W/cm-°C to 0.147 (~ 50% decrease) and in the axial direction (tube length) to 0.281 (10% decrease). In the radial direction, the presence of the oxide film is of considerably greater significance than the probable error in the measured thermal conductivity data for Zircaloy-4.

304 SS - The thermal conductivity of 304 SS was measured by Ewing, et. al.⁽³⁹⁾, using an absolute method, from about 100° to 725°C and the data are presented in Figure 10. The curve fits Ewing's data within ± 1 percent. However, in the 600° to 725°C range, Ewing's curve indicates a significant increase in slope (dk/dT) and it is not recommended for extrapolation to higher temperatures. Ewing also measured the thermal conductivity of two heats of 310 SS in the temperature range of 100° to 575°C with a precision such that the data could be represented by two straight lines with a maximum deviation of less than ± 1 percent for each heat. The difference in the conductivity between the two heats was about 2 percent. The data of Ewing indicate an extreme precision and reproducibility of measurement. Shelton⁽⁴⁰⁾ measured the thermal conductivity of five 18-8 stainless steels in the temperature range of 100° to 500°C relative to a lead heat meter with a reported precision of $\pm 2\%$. He indicated that the absolute thermal conductivity of lead was known to $\pm 3\%$. The chemical compositions of two of the five steels fall within current specifications for 304 SS. The values for the two steels were about 3 percent lower than Ewing's values over the common temperature range. Some of the data points from Shelton's measurements fall on Ewing's curve.

The Thermophysical Properties Research Center (TPRC)⁽⁴¹⁾ compiled and evaluated the thermal conductivity data on a large number of stainless steels, a number of which were designated 304 SS and others of the general

18-8 class. The recommended values designated as representing 304 SS are also shown in Figure 10. The data above 725°C were obtained by extrapolation. The TPRC data were estimated to be within $\pm 5\%$ from $\sim 30^\circ$ to $\sim 625^\circ\text{C}$ and $\pm 10\%$ of the true value for 304 SS above $\sim 1100^\circ\text{C}$.

The TPRC composite curve did not include Ewing's data. However, as can be noted, the difference at 625°C is only $\sim 1\%$. Both Ewing and Shelton showed outstanding precision in their measurements and both showed that minor differences in composition led to differences in conductivity of 2 to 3% for nominally the same materials. For this reason, the TPRC data, representing an average value for thermal conductivity of 18-8 stainless steels having a composition in the 304 SS range, are recommended.

As in the case of Zircaloy-4, an oxide film will form on the 304 SS at high temperatures in the presence of steam. The composite material will have a lower conductivity than the 304 SS. The thermal conductivity of NiO has been estimated as 0.15 to 0.047 W/cm-°C in the temperature range of $\sim 75^\circ$ to $925^\circ\text{C}^{(41)}$. A room temperature value of 0.07 W/cm-°C was found for $\text{Fe}_3\text{O}_4^{(41)}$. The precision of the data for both materials was indicated as $\pm 10\%$.

The thermal conductivity of the mixed oxide in the temperature range above 1000°C may be comparable to that of ZrO_2 and therefore the effect of a 50-micron-thick oxide layer on a tube with a 0.051 cm wall thickness would be similar to that indicated for the Zircaloy-4.

UO₂ - A critical evaluation of the thermal conductivity of UO₂ was made by an IAEA Panel in April 1965. The following discussion is extracted (part verbatim) from the conclusions⁽⁴²⁾ of the Panel.

Unirradiated UO₂ - From 200° to 1300°C, the thermal conductivity of 95-percent-dense polycrystalline UO_{2.005} can best be represented by

$$k = \frac{1}{11.75 + 0.0235t} \quad \text{W/cm-}^{\circ}\text{C},$$

where t is temperature in °C.

Above 1300°C, the reported values for thermal conductivity do not agree⁽⁴³⁻⁵¹⁾. This has been attributed to specimen compositional changes occurring at high temperatures and to experimental problems in measuring thermal conductivities at high temperatures. However, many data indicate that the thermal conductivity of unirradiated UO₂ increases with increasing temperatures above 1400°C⁽⁴⁶⁻⁴⁹⁾. The high temperature thermal conductivities measured or deduced from in-reactor experiments do not generally agree with conductivities measured out-of-reactor, in that in-reactor tests show little or only a moderate increase in conductivity at high temperatures.

a. Effect of Density - The density correction for the thermal conductivity of UO₂ can be expressed by

$$k_A = k_B \left(1 + \beta \frac{\rho_A - \rho_B}{\rho_B} \right)$$

where k_A and k_B are the thermal conductivities at densities ρ_A and ρ_B , respectively, and β is a parameter that depends upon the characteristics of the oxide. For polycrystalline UO_2 , β can vary between 1 and 4 depending upon the microstructure and other properties of the oxide; the recommended value is 2.5.

b. Effect of O/U Above 2.000 - An increase in the O/U ratio above 2.000 decreases the thermal conductivity as shown in Figures 11 and 12. It is estimated⁽⁴²⁾ that at 60°C the conductivity decreases approximately 4 percent for each incremental increase of 0.01 in the O/U ratio, and 2 - 10% for each 0.01 increase in O/U at 920°C as shown in Figure 11⁽⁵⁰⁾. The absolute accuracy of data in Figure 11 is not known. The data in Figure 12 were obtained from four different investigations and are shown here to illustrate the very significant effect of excess oxygen on the thermal conductivity of UO_2 .

Irradiated UO_2 - Stoichiometric, polycrystalline UO_2 irradiated at temperatures greater than 500°C does not show a decrease in the post-test low-temperature thermal conductivity. In contrast, UO_2 irradiated at temperatures below 500°C shows a marked decrease in the low-temperature thermal conductivity. At exposures of $\sim 3 \times 10^{19}$ fissions/cm³, this damage can be wholly or partially removed by high-temperature annealing; whereas, at high exposures, little or no recovery occurs.

Using grain size and molten boundary measurements to define the radial temperature profile of reactor tested fuel pins, Lyons et. al.^(43,52) derived values for the thermal conductivity of UO_2 as a function of temperature to 2800°C . By experiment,

$$\int_{0^\circ\text{C}}^{2800^\circ\text{C}} k dT = 86 \text{ or } 90 \text{ watts/cm.}$$

The values of k as a function of temperature are presented in Figure 13. The data for both values of $\int k dT$ are in excellent agreement with the values recommended by the IAEA Panel⁽⁴²⁾ from 800° to 1300°C . In the lower (200° to 800°C) range, the values derived for the lower value of the integral are about 5% lower than the IAEA recommended values. The conductivities derived from both integrals tend to increase with temperature above $\sim 2000^\circ\text{C}$. However, the increase is much less than that indicated by the results of other investigators^(46,49). The reason for this is not known. In Feith's work, the measurements were made in hydrogen and on cooling the sample powdered, presumably because of hydriding. It is known that hypostoichiometric urania has a higher conductivity than UO_2 at low and intermediate temperatures.

In the loss-of-coolant incident, the UO_2 which has operated below 1600° to 1800°C will tend to increase in porosity as the temperature increases above its normal operating level and oxidize when the clad fails (melts, ruptures, or completely oxidizes). Both of these effects will decrease

the thermal conductivity. In addition, the clad envelope may increase in diameter at the higher temperatures because of gas pressure and the resulting gap will also result in a lower "net" conductivity of the fuel pin. From these considerations, any large increase in "effective" UO_2 conductivity appears remote. Therefore, the data derived for a conductivity integral of 86 watts/cm and shown in Figure 13 are recommended for use in loss-of-coolant calculations.

ZrO_2 - Conductivity values for pure (unstabilized) ZrO_2 are not available, probably because of specimen damage due to the phase change near 1100°C . Data at high temperatures have, however, been published for ZrO_2 stabilized with CaO , MgO , or Y_2O_3 . Data for low (66%) density, 4%- CaO -stabilized, material⁽⁴⁷⁾ in Figure 14 show a rapid increase in conductivity above 1700°C , which is probably due to radiant heat transfer, particularly across voids within the material. Below 1400°C this curve (corrected to theoretical density) is in good agreement with the results of Kingery for CaO -stabilized ZrO_2 ⁽⁵³⁾. Conductivity of high density (97%) material of the composition 80% ZrO_2 , 12% Y_2O_3 , 8% Zr ⁽⁴⁷⁾ agrees reasonably well with that of the low density material up to 1700°C but does not show the rapid increase above this temperature. Data for 85% ZrO_2 , 15% Y_2O_3 at 86.7% density⁽⁵⁴⁾ are also shown in Figure 14. Before plotting, all data were corrected to 100% density by dividing measured conductivities by fractional porosity.

The data for ZrO_2 (Y_2O_3 , Zr) are recommended.

11. Enthalpy and Heat Capacity

Zircaloy-2 - Data for two forms of Zircaloy-2 (standard and low nickel content) were obtained by Eldridge and Deem⁽²²⁾. They found a heat effect of 3.5 kcal/g-atom at about 635°C which they attributed to a change in tin solubility at this temperature. The low-nickel alloy gave similar results.

UO₂ - Enthalpy of UO₂ from 25° to 1200°C is well represented by the data of Moore and Kelley⁽⁵⁵⁾. The most complete data at higher temperatures, from 900° to 2840°C, are those of GE-NMPO⁽¹⁶⁾, which are shown in Figure 15. In the temperature range of overlap of the equations from these sources, the maximum disagreement in enthalpy and in heat capacity is less than 2%. Recent measurements by Ogard and Leary⁽⁵⁶⁾ up to 2000°C are in reasonable agreement with these results. Moore and Kelley's data were combined with GE-NMPO data to 2350°C by Godfrey et. al.⁽⁵⁷⁾ to produce a fifth order polynomial expression for enthalpy over the range 210° to 2350°C.

However, the equation in Table I, containing the exponential term, is a better representation of the data from 900° to 2840°C and is recommended in this range.

B. Mechanical Properties

Selected values for tensile strength, modulus of elasticity, and ductility for Zircaloy-2 or -4, 304 stainless steel, UO₂, and ZrO₂ are summarized in Figures 16 to 19 and/or presented in Table II. Where pertinent, these data are discussed.

1. Tensile Strength

Zircaloy-4 - The unirradiated tensile strength properties of Zircaloy-2 and -4 are well defined up to $\sim 500^{\circ}\text{C}$, the limit of engineering usefulness in BWR and PWR applications. Very limited data are available at temperatures above $\sim 500^{\circ}\text{C}$.

The values for yield and ultimate tensile strength and the total elongation at fracture are highly dependent on the amount of cold work (CW) remaining in the material at the particular test temperature. For example⁽⁵⁸⁾, the room temperature tensile strength for 78% CW + 510°C stress-relieved Zircaloy-4 tubing is 78.7 kg/mm^2 , compared to 57 kg/mm^2 for 78% CW + 650°C annealed material, a difference of ~ 40 percent. At 510°C , the tensile strength of annealed Zircaloy-4 is about 50 percent less than that of the cold worked material. At temperatures $\geq 600^{\circ}\text{C}$, the effects of cold work are rapidly annealed and the difference in strength between the cold-worked and annealed materials is essentially eliminated.

In addition to the effect of cold work on the strength properties of Zircaloy-4 tubing, there may also be a difference between the longitudinal and circumferential strength properties. In general, at room temperature the transverse tensile strength of Zircaloy-2 plate, with up to 70% CW, is 90 - 100 percent of the longitudinal⁽⁵⁹⁾. Transverse tensile tests, using a ring type specimen, on Zircaloy-4 tubing with $> 70\%$ CW show a 10 - 20 percent lower room temperature transverse strength than the

longitudinal strength⁽⁵⁸⁾. For annealed tubing, the difference in transverse (ring test specimens) and longitudinal strength does not appear to be significant up to at least 500°C. However, using internal pressure⁽⁵⁸⁾ on annealed tube sections, the transverse strength was 10 to 20 percent higher than the longitudinal strength for temperatures up to about 350°C. Regardless of prior history, the difference between transverse and longitudinal strength is not significant at temperatures of ~ 600°C or higher.

In summary, while there are marked differences in the strength between cold-worked and annealed Zircaloy at low temperatures, above about 500°C this difference rapidly decreases until, at temperatures of concern to a loss of coolant incident, the effects of cold work on strength properties may be considered to have been eliminated. In addition, as will be discussed later, irradiation markedly increases the strength of the annealed material and at high ($\sim 2.5 \times 10^{21}$ nvt) fluence levels the unirradiated strength differences between annealed and cold worked material are practically eliminated at temperatures even below 500°C.

The tensile strength at temperatures up to 1800°C (50°C below the melting point) of annealed Zircaloy-4 sheet specimens⁽³⁰⁾, with the load applied in the rolling direction (longitudinal), is presented in Figure 16. Tests at room temperature were performed at a strain rate of 0.005 min^{-1} and at elevated temperatures at a strain rate of 0.06 min^{-1} . The values for the annealed sheet specimens are in excellent agreement with those for annealed tubing.

Irradiation at BWR and PWR nominal operating conditions (temperature-pressure) raises the tensile strength of both the annealed and cold-worked material. Bement⁽⁶⁰⁾ reports results on specimens (gage section 0.25 cm x 0.5 cm x 5.5 cm) fabricated from Zircaloy-2 plate with cold work up to 70 percent. The material was irradiated in the ETR G-7 pressurized water loop ($\sim 280^{\circ}\text{C}$ water temperature, 288° to 304°C specimen temperatures) to a fluence* of $2.5 \times 10^{21} \text{ n-cm}^{-2}$. At this fluence, the 0.2 percent yield strength at 300°C for the annealed material was 46.1 kg/mm^2 as compared to the pre-irradiated value of 13.1 kg/mm^2 ; the 40-percent-cold-worked material was 48.5 kg/mm^2 vs a pre-irradiated value of 39.3 kg/mm^2 . The 0.2 percent yield strength in the transverse direction was a few percent higher than the longitudinal at all fluence levels above about $10^{19} \text{ n-cm}^{-2}$.

Tensile tests at temperatures up to 370°C have been performed using ring sections of 78% CW Zircaloy-4 tubing from a fuel rod and from a section of unfueled tubing, irradiated in water at $\sim 290^{\circ}\text{C}$ to fluences up to $10^{21} \text{ n-cm}^{-2}$ ⁽⁵⁸⁾. The tensile strengths** of the tubing at 300°C are in good agreement with Bement's data for $\sim 10^{21} \text{ n-cm}^{-2}$. The results of the ring tests at room temperature, 290° and 370°C are also shown in Figure 16.

*Unless otherwise stated, all fluence values in this report are based on $E > 1 \text{ Mev}$.

**A yield strength as determined in the ring test is not considered valid. Because Bement's 0.2% yield strength and tensile strength values for material irradiated to $4 \times 10^{19} \text{ n-cm}^{-2}$ are approximately the same, it is believed that comparing the Westinghouse tensile strength results with Bement's is valid.

In a loss-of-coolant incident, as the temperature rises the effects of irradiation may be greatly reduced by thermal annealing. Howe and Thomas⁽⁶¹⁾ studied the recovery of both annealed and 25.5-percent-cold-worked Zircaloy-2, irradiated at 280°C in water up to $2.7 \times 10^{20} \text{ n-cm}^{-2}$. The specimens were annealed 1 hour at temperatures from 350°C to 700°C, then tested at room temperature. At the highest fluence ($2.7 \times 10^{20} \text{ n-cm}^{-2}$) the radiation-induced strength increase was eliminated at temperatures above 500°C for both annealed and 25.5-percent-cold-worked material. The cold-worked material recovered at $\sim 450^\circ\text{C}$, and in all cases there was significant recovery at temperatures as low as 350°C. Howe's data also indicate that the annealing temperature required for complete recovery increases with increasing fluence. In contrast to the 350°C annealing results of Howe, Bement's⁽⁶⁰⁾ results on annealing of Zircaloy-2, irradiated to fluence levels ranging from 1×10^{20} to $2.5 \times 10^{21} \text{ n-cm}^{-2}$ at 288°C to 304°C, showed essentially no recovery after a 10-hour anneal at 360°C. Bement suggests that this increase in stability of radiation effects may be the result of small differences in flux rate and irradiation temperature around 300°C. While the available data indicate that the threshold annealing temperature and the temperature required for complete annealing are somewhat dependent on irradiation temperature and total fluence, it is expected that at low heating rates (0.3°C/sec) much, if not all, of the radiation-induced strengthening at fluence levels up to at least $10^{21} \text{ n-cm}^{-2}$ will be annealed at temperatures in the range of 500°C to 700°C. As the heating rates increase, the temperature for a

given amount of annealing will increase. Present available data on the annealing kinetics are not sufficient to accurately predict the times required to anneal a given amount of the radiation-induced strengthening as a function of temperature.

304L Stainless Steel - There is a large volume of tensile strength data for 304L stainless steel for temperatures up to about 700°C, but only very limited data above this temperature and essentially none at 1000°C and above. Tensile strength data obtained from tube burst testing are extremely limited and the highest temperature for which data are available is about 900°C.

As noted for Zircaloy-4, the strength and ductility properties are very sensitive to the amount of cold work remaining in the material at the particular test temperature. However, contrary to the case for Zircaloy-4, there is very little difference in strength properties in the longitudinal and transverse directions. The tensile strength is somewhat insensitive to strain rate in the temperature range up to about 600°C. However, at temperatures of 600°C and above, strain rate has a significant effect on the strength and ductility values for the material. Data of Martin and Weir⁽⁶²⁾, tabulated below, illustrate the above point.

Test Temperature, °C	Strain Rate ($\dot{\epsilon}$) min ⁻¹	Tensile Strength, ksi	Total Elongation 1" Gage Length, %
704	0.002	24.4 (3) ¹	40 (3)
	0.02	30.5 (3)	53 (3)
	0.2	36.5 (3)	45 (3)
843	0.002	11.4 (2)	34 (2)
	0.02	14.8 (3)	46 ² (2)
	0.2	19.3 (1)	52 (1)

1. Strength and ductility values are the average for No. of specimens, e.g., (3).
2. Value of 25.1% for one specimen not included.

As can be noted at 704°C, changing the strain rate from 0.002 min⁻¹ to 0.02 min⁻¹ changes the measured strength by about 25 percent. The data are also shown in Figure 17. Similar strain-rate effects were obtained on material irradiated to a fluence of 7×10^{20} n-cm⁻² ($E_n \geq 1$ Mev) and 9×10^{20} n-cm⁻² ($E_n = \text{thermal}$).

The tensile strength of 304L SS, in the annealed^(63,64,65) and 25-percent-cold-worked⁽⁶⁶⁾ condition, as a function of temperature is presented in Figure 17. The solid line for the unirradiated material represents the GE-NMPO⁽⁶³⁾ data from room temperature to 1375°C ($\sim 25^\circ\text{C}$ below the solidus for annealed 304L stainless steel). As may be noted, the agreement among the 3 sets^(62,63,64) of data for the annealed material is excellent over the common temperature ranges.

In addition to the axial tensile data, biaxial or tube burst data⁽⁶⁵⁾ are also shown for temperatures from 500° to 900°C. These tests were performed⁽⁶⁶⁾ in argon, also using argon to pressurize the tubes. The time from the start of pressurization to failure normally ranged from one to two minutes. The strain rate in these tests was variable; but based on time from start of pressurization to failure and the diametral strain at failure, the strain rate ranged from about 0.1 to $\sim 0.2 \text{ min}^{-1}$. As may be noted, there is good agreement with Martin and Weir's data⁽⁶²⁾ at 704° and 843°C for a strain rate of 0.2 min^{-1} . The tensile strength of 304L with 25 percent cold work⁽⁶⁷⁾ is also shown in Figure 17. The strength of the cold worked material decreases rapidly above 500°C and is essentially the same as for the annealed at about 800°C.

Irradiation increases the strength of both the cold-worked and annealed material. The data for sheet material shown in Figure 17 are for material irradiated in the G-7 pressurized-water loop in the ETR. The loop operates at about 280°C and 1.41 kg/mm^2 , temperature and pressure conditions comparable to a PWR or BWR. Irradiation of annealed material to a fluence of $6 \times 10^{21} \text{ n-cm}^{-2}$ ($E_n > 1 \text{ Mev}$) increases the strength⁽⁶⁸⁾ markedly for temperatures below 500°C; however, above 500°C the effects of irradiation on tensile strength are rapidly eliminated and at 600° to 750°C the strength of the irradiated material is almost identical to the unirradiated. A similar behavior is observed for the cold-worked material.

The tube-burst data for irradiated material were obtained in a manner similar to that described for the unirradiated tubing⁽⁶⁶⁾. The tubing was taken from fuel pins used in the EBR-II sodium-cooled reactor. The irradiation temperatures and fluence vary along the length of the tube; the temperature of irradiation ranged from $\sim 371^{\circ}$ to 517°C and the fluence from 5×10^{21} to 1.2×10^{22} n-cm^{-2} ($E_n > 1 \text{ Mev}$).

It may be fortuitous, but the strength data from these tube burst tests are in good agreement with the axial tensile data obtained from material irradiated in an environment very similar to that of PWR or BWR. In addition, the data indicate that at 800° and 900°C the strength of the irradiated material is 20 to 25 percent lower than the strength of the unirradiated material.

UO₂ - The equation given in Table II is for modulus of rupture instead of axial tensile strength. Considering the gross changes that occur in the as-fabricated microstructure of UO₂ as a result of the high center-line operating temperatures, as well as the very high radial temperature gradient in the fuel, it is extremely doubtful that the as-fabricated strength values for UO₂ are of value. The fact that the UO₂ probably will be cracked both transversely and axially must also be considered in use of any strength data for this material.

ZrO₂ - All high-temperature strength data on ZrO₂ are for stabilized or partially stabilized material and are of questionable value for loss-of-coolant calculations.

2. Ductility

The ductility of the cladding can be of considerable importance in determining the behavior of the core in the initial and intermediate temperature portion of the loss-of-coolant incident. If the ductility of the clad is extremely low, there is the possibility that stresses developed during the blow-down phase may result in considerable fracturing of fuel pins and early disruption of the fuel coolant channels, with a consequent restriction of steam flow to the upper portions of the core. In the event that the cladding cracks, the internal gas pressure will be relieved and reduce the possibility of the tubes being expanded at higher temperatures where ductility may be increased. A considerable amount of ductility information from axial tensile tests is available for both Zircaloy-4 and 304L stainless steel in the low temperature range ($\leq 500^{\circ}\text{C}$ for Zr-4, $\leq 800^{\circ}\text{C}$ for 304L SS). However, what is most pertinent for the loss-of-coolant condition is the biaxial ductility as obtained from tube burst testing. Data for total circumferential elongation or diametral expansion at rupture are extremely limited or not available for irradiated material.

Zircaloy-4 - Total elongation as a function of temperature for tubing and sheet material is presented in Figure 18. Below about 400°C , the ductility

is essentially independent of temperature; however, between 360° and 480°C there is a substantial increase in circumferential elongation in the tube burst tests for the 78 cold worked + 650°-annealed material. In burst tests on the cold-worked material, the circumferential elongation increased only slightly between 300° and 530°C ($\sim 200^\circ\text{C}$ above normal operating temperature in BWR's and PWR's).

Irradiation under BWR and PWR conditions of pressure and temperature lowers the ductility of both the cold-worked and annealed materials. There is a large volume of data for ductility at 300°C and fluences up to $\sim 10^{22} \text{ n-cm}^{-2}$, as derived from tensile tests on sheet or plate material, in both the longitudinal and transverse directions. At 300°C, the total transverse elongation of Zircaloy-2 decreases from ~ 30 percent to less than 10 percent at $1 \times 10^{20} \text{ n-cm}^{-2}$; to less than 5 percent at $2.5 \times 10^{21} \text{ n-cm}^{-2}$, and appears to remain in the range of 3 to 4 percent up to $\sim 10^{22} \text{ n-cm}^{-2}$ (69).

Annealing at 450°C for one hour completely removed the decrease in ductility in both annealed and 25.5% cold worked Zircaloy-2 irradiated to $2.7 \times 10^{20} \text{ n-cm}^{-2}$ at 280°C in water (61). Data for the effects of annealing at temperatures above 400°C for Zircaloy irradiated to fluences above the $2.7 \times 10^{20} \text{ n-cm}^{-2}$ were not found. However, while much of the low temperature ($< 500^\circ\text{C}$) ductility decrease for irradiated material is recovered by annealing at temperatures as low as 500°C, the effect of irradiation on the ductility at high temperatures ($> 500^\circ\text{C}$) is not

known. As will be indicated later, annealing of irradiated 304L stainless steel at 900°C restored the ductility up to about 500° - 600°C but at 800° - 900°C, there was little or no improvement in ductility after annealing.

304L Stainless Steel - Total elongation as a function of temperature for 304L stainless steel in the annealed, 25-percent-cold-worked, and irradiated conditions, is presented in Figure 19. The solid curve for the annealed unirradiated material represents the GE-NMPO data⁽⁶³⁾ for temperatures up to 1375°C ($\sim 25^\circ\text{C}$ below the solidus for 304L SS). Shown for comparison are data from Martin and Weir⁽⁶²⁾ and BNWL⁽⁷⁰⁾. As may be noted, there is good agreement over the common temperature ranges. Cold work causes a large reduction in ductility at the lower temperatures, but at the higher temperature the total elongation approaches that of the annealed material⁽⁷⁰⁾.

Elongation values for tube-burst tests⁽⁶⁵⁾ are also presented in Figure 19 for temperatures in the range of 600° to 900°C. The data were obtained on tubes 0.44-cm O.D. with a 0.023-cm wall thickness⁽⁷¹⁾ in the annealed condition. Testing was performed as described under Tensile Strength. The values presented are percent diametral expansion. As can be noted, the values are much lower than are values from the uniaxial tests.

Irradiation progressively lowers the ductility of both the cold-worked and annealed material. The data⁽⁷⁰⁾ shown in Figure 19 are for annealed 304L transverse specimens irradiated in the ETR G-7 pressurized water loop at

$\sim 290^{\circ}\text{C}$. At 700°C the ductility for the unirradiated 25-percent-cold-worked and the annealed irradiated $1 \times 10^{21} \text{ n-cm}^{-2}$ ($E_n \geq 1 \text{ Mev}$) are about equal.

At higher fluence levels the elongation is further reduced, being less than 2 percent⁽⁷²⁾ at 750°C for $\sim 6 \times 10^{21} \text{ n-cm}^{-2}$ ($E_n \geq 1 \text{ Mev}$).

Percent diametral expansion for 304L tubing from EBR-II fuel elements (test procedures and irradiation condition as previously discussed under Tensile Strength⁽⁶⁵⁾) range from less than one percent to about 3.5 percent in the temperature range 600° to 900°C . Annealing of the irradiated tubing for one hour at 900°C resulted in recovery of the pre-irradiated ductility at test temperatures of 600° and 700°C but showed no effect on the 800° and 900°C values.

3. Compressive Strength

High-temperature data were found only for ZrO_2 (stabilized with MgO).

4. Modulus of Elasticity

In Table II, modulus of elasticity is expressed as a linear function of temperature for the metals, and as individual values at several elevated temperatures for the oxides.

Discussion

These data on the strength and ductility of Zircaloy-4 and 304L stainless steel have been presented and discussed without consideration of the effects on these properties of exposure, at high temperatures, to the

steam-hydrogen environment produced in the loss-of-coolant incident. The overall effects of the steam environment on the Zircaloy-4 will be discussed in reference to the data on pressurized tubes heated at $0.3^{\circ}\text{C}/\text{sec}$ tabulated below.

Effect of Internal Pressure on the Maximum Temperatures Attained Prior to 34 Percent Expansion on Zircaloy-4 Tubing^a Heated at $0.3^{\circ}\text{C Sec}^{-1}$ in Ar + 3% H₂ and in Steam⁽⁶³⁾.

Internal Gage Pressure kg/mm ²	Maximum Temp. $^{\circ}\text{C}^b$		Diametral Expansion ^b %	
	Ar + 3% H ₂	Steam	Ar + 3% H ₂	Steam
0.040 (57) ^c	1180	1475	33	12.5 ^d
0.057 (81)	1055	1460	34	11.4 ^d
0.077 (110)	970	1035	34	18.6 ^d
0.141 (200)	905	905	34	33

^a 1.35 cm OD x 0.076 cm wall, annealed condition.

^b The tube sections were heated by induction. When the diametral expansion reached 32 to 34% the induction field was shorted and the test terminated.

^c Numbers in parentheses are pressure in psi.

^d Tube failed with multiple cracks.

In the argon-hydrogen atmosphere, all tests were terminated by the tube expanding 34 percent; in steam at pressures of 0.077 kg/mm^2 (110 psi) or less the tube failed by cracking after an expansion of about 1/2 or less of the expansion at the highest pressure. In addition, for the two lower pressures in steam, the temperatures reached before failure were 300° to 400°C higher than in the Ar + H₂ atmosphere. These higher temperatures for failure indicate a considerable strengthening of the material and loss

of ductility by the steam oxidation. At higher pressure (0.141 kg/mm^2), the rate of expansion with increasing temperature is sufficiently high that the limiting expansion of 34% is attained at 905°C in both atmospheres, indicating that the time-temperature combination was not sufficient for steam oxidation to produce a significant effect. At higher heating rates, the temperatures for a given expansion increase with an increase in heating rate; an increase in pressure lowers the temperature at which a given expansion occurs. The effect of the steam atmosphere is to lower the expansion rate at a given pressure-heating rate condition. The presence of steam probably does not have a significant effect at temperatures up to 1000°C on the expansion rate for pressures above $\sim 0.1 \text{ kg/mm}^2$ with heating rates of 3.0°C per second or greater. One important effect of steam may be that the tube will expand more uniformly; that is, oxidation will tend to work harden the Zircaloy-4 and tend to prevent instability (high localized expansion) in the tube.

The overall significance of the low strength and high ductility of Zircaloy at elevated temperatures (assuming that irradiation effects on ductility are annealed rapidly at temperatures $\sim 700^\circ\text{C}$ and above) is that the fuel bundle coolant passage area may be greatly reduced by tube expansion even in a steam atmosphere.

The effects of the steam environment on the 304L stainless steel as a function of temperature are much different from those of Zircaloy-4. The parabolic rate constant for the reaction (oxidation) at 1000°C of 304L

stainless steel in steam is about a factor of 15 lower than for Zircaloy-4. However, the activation energy for the steam-304L SS reaction is much greater than for Zircaloy-4, and at about 1200°C the rate of oxidation of the stainless steel is slightly greater than for Zircaloy-4. The stainless steel has a very low solubility for oxygen in comparison to the Zircaloy-4, and the ductility (expansion) will not be significantly changed in the temperature range up to 1000° to 1100°C at slow to moderate heating rates (0.3° to 3°C/sec). There will be less change as heating rate increases. Another significant factor is the difference in strength, the stainless steel being about 4 to 8 times stronger than Zircaloy-4 in the 700°C to 1200°C range. In addition, the available ductility data from tube-burst tests for the 304L SS and Zircaloy-4 tubing show the annealed Zircaloy-4 burst ductility to be much greater than for the 304L SS tubing. Furthermore, it appears that at ~ 500°C considerable annealing of the irradiated Zircaloy-4 occurs and the pre-irradiated ductility may be recovered. This does not appear to be the case for the 304L SS.

For a given internal gas pressure in the tubing (due to burnup), the net effect of the above factors will be that the 304L SS will swell much less than the Zircaloy-4; in fact, based on the low (~ 3 percent) diametral expansion of irradiated 304L SS tubing on fracture at 900°C, it appears that there will be a limited reduction in fuel bundle coolant passage area before fracture or perforation of the 304L SS tubing would occur.

IV. REACTION KINETICS OF FUEL ELEMENT MATERIALS

The initial reaction occurring as the core experiences a thermal transient upon loss of coolant will be oxidation of the metallic cladding. In addition, as the temperature increases, Zircaloy-4 may react with the UO_2 , but no significant reaction is anticipated between 304 SS and UO_2 . If the metal oxidation is appreciable, the oxidized metals in both cases can react with the UO_2 to form mixed oxide compositions of lower melting points. This situation will also be complicated by the oxidation of the UO_2 . The various reactions are discussed below.

A. Zr (OR ZIRCALOY-4) WITH STEAM AND/OR AIR

The most important and the most thoroughly studied reaction is that of Zr (or Zircaloy-4) with water vapor. This reaction can be expressed by the equation:

The kinetics of the oxidation of Zr are affected by diffusion of oxygen through oxide layers of continuously increasing thickness, variable composition, and three possible crystallographic structures, as well as into metal of two structures in which up to 29.7 atom percent oxygen is dissolved. Therefore, it is very probable that the logarithm of the oxidation rate of Zircaloy-4 is not linearly related to reciprocal absolute temperature; that is, the apparent activation energy of the oxidation process is not independent of temperature.

Two studies have been reported in which the reaction kinetics of H_2O with solid Zircaloy-2 at high temperatures were determined by measuring the evolved H_2 . Bostrum⁽⁷³⁾ inductively heated metal cylinders immersed in water to temperatures ranging from 1300° to about $1860^\circ C$. Lemmon⁽²⁹⁾ exposed metal samples to steam at fixed temperatures in the range from 1000° to $1690^\circ C$. Both of these studies showed approximately parabolic reaction rates. However, the rates disagreed above $1300^\circ C$; Lemmon reported an activation energy of 34 kcal/mole compared to 65 kcal/mole for Bostrum's data.

Baker and Just⁽⁷⁴⁾ have correlated the data of Lemmon and Bostrum with their own results, which were obtained from measurement of the oxidation rate at the melting point of Zircaloy-2 by a condenser-discharge technique. Using the oxidation rate at the melting point and the lower temperature data of Lemmon and Bostrum, they calculated a rate which can be expressed as follows:

$$W^2/t = 4.10 \times 10^6 \exp \frac{-45,500}{RT} \text{ mg}^2/\text{cm}^4\text{-sec}$$

where W is the weight gain (oxygen pickup) per unit surface area in mg/cm^2 , t is time in seconds, R is the gas constant in cal/mole, and T is the absolute temperature.

GE-NMPO data on isothermal rates⁽⁷⁵⁾ from 1200° - $1600^\circ C$ coupled with Lemmon's low temperature data give the equation, applicable from 1000° - $1600^\circ C$:

$$W^2/t = 7.10 \times 10^5 \exp \frac{-40,500}{RT} \text{ mg}^2/\text{cm}^4\text{-sec}$$

This is shown in Figure 20 with the 95% confidence bands and the data referred to above. Essentially all of these data, with the exception of Bostrum's 1600°C point (which is high) and Lemmon's points between 1400° and 1700°C (which are low), fall within the 95% limits of this equation.

Figure 20 also shows more recent GE-NMPO data above 1600°C⁽⁷⁵⁾ which deviate from the lower temperature data but show good agreement with Baker's point, and fair agreement with Bostrum's 1750°C point.

Thus, for one or more of the reasons mentioned earlier, there is evidence that a higher-activation-energy process controls oxidation near the melting point. For simplicity the oxidation rate in the range 1000° - 1600°C can be represented by the GE-NMPO-Lemmon equation above; while from 1600°C to the melting point the following equation, also shown in Figure 20, is recommended:

$$w^2/t = 1.5 \times 10^8 \exp \left(\frac{-60,600 \pm 5400}{RT} \right)^{(75)}$$

During a thermal excursion, the extent of oxidation of the Zircaloy will depend upon the rate of temperature increase and the amount of steam and/or air available. Reaction in air at 1200° - 1600°C is 2 to 4 times as rapid as in steam because of formation of ZrN⁽⁶³⁾.

B. TYPE 304 SS WITH STEAM AND/OR AIR

Recent kinetic measurements⁽⁷⁵⁾ show that the reaction between 304 SS and steam proceeds relatively slowly at low temperatures, but that the rate equals the rate for Zr in steam at 1200°C and exceeds it above this temperature.

The recommended equation for calculating the rate of weight gain due to oxidation of 304 SS in steam at temperatures above 1000°C is:

$$W^2/t = 2.4 \times 10^{12} \exp \left(\frac{-84,300 \pm 2400}{RT} \right) \text{ mg}^2/\text{cm}^4 \text{ sec (See Figure 21)}^{(75)}$$

Although the weight gain was observed to be linear with time in the early stages of oxidation, no appreciable error is introduced in calculating total weight gain from the above equation representing parabolic behavior.

Oxidation of 304 SS in dry air is slower by a factor of ~ 1000 at temperatures below 1370°C because of the formation of a protective Cr_2O_3 layer. Above 1370°C, however, the rate in air equals that in steam and the oxide formed is frothy and shows signs of melting. The equation for steam oxidation thus represents a conservative analysis for air oxidation as well.

C. UO₂ WITH STEAM AND/OR AIR

The rate of oxidation of UO₂ in steam at temperatures from 900° to 1835°C has been studied⁽⁷⁵⁾, and found to be represented by the equation

$$W^2/t = 8.4 \times 10^4 \exp [(-48,000 \pm 1900)/RT] \text{ mg}^2/\text{cm}^4\text{-sec.}$$

The maximum O/U ratio expected in steam oxidation is the ratio in equilibrium with steam, which varies from 2.20 at 1200°C to 2.16 at 1800°C.

In the absence of air, therefore, only the UO_{2+x} phase should be present.

Although the lattice parameter of this phase decreases with increasing oxygen content (density increases), fission gas pressure at high temperatures (> 2000°C) may generate voids accompanied by an increase in volume.

As indicated previously, a secondary effect of UO_2 oxidation is a lowering of the melting point^(11,12).

UO_2 will oxidize in air at 900°C to $\text{UO}_{2.67}$ and to lower O/U ratios at higher temperatures⁽⁷⁶⁾. At 1300°C , the limiting composition is $\text{UO}_{2.61}$ ⁽⁷⁷⁾. These compositions exist in the U_3O_8 orthorhombic structure, which at the stoichiometric composition has a density of 8.39 g/cc compared to 10.96 g/cc for UO_2 , indicating a large volume increase on oxidation in air.

Above 1350°C , evaporation in air as UO_3 is fairly rapid.

D. CLADDING METAL WITH UO_2

Zircaloy-4

The corrosion rate of the Zircaloy - water reaction suggests that molten metal probably will be in contact with the UO_2 as the temperature excursion proceeds past the melting point of the metal (about 1850°C in the case of low oxygen-content metal and about 1950°C in the case of oxygen-saturated metal). Thermodynamically, it is reasonable to expect that Zr will reduce UO_2 ; the fact that this occurs at temperatures as low as 700°C is reported by Mallett, et. al.⁽⁷⁸⁾. Recent qualitative tests above 1900°C indicate that the reaction rate is relatively rapid at 2300°C . It should be noted, however, that this reaction releases only a relatively small amount of heat.

Thus, the Zircaloy metal with or without dissolved oxygen will react with the UO_2 to form ZrO_2 . Intermediate reactions will probably yield the

ZrO_{2-x} and the Zr-U solid solutions⁽⁷⁸⁾. Since these intermediate mixtures of U and Zr have lower melting points than Zr, the result will be the formation of some U-containing liquid phase at the Zr- UO_2 interface. This effect will obviously be most pronounced when the Zr is least oxidized.

The UO_2 - ZrO_2 phase equilibrium diagram is shown in Figure 22 to illustrate the liquidus temperatures and phases to be expected at temperatures below the melting point of UO_2 when the two oxides have reacted. Since the Zr-U phase equilibrium diagram shows these two metals as a complete series of solid solutions, that phase diagram is not included. There are no available data on the phase equilibrium systems involving the ZrO_{2-x} , UO_{2-x} , and UO_{2+x} compounds. However, the melting points of UO_{2+x} compositions vary, depending on the oxygen present, as shown in Figure 1.

304 SS

The reactions expected with Type 304 SS will be dependent upon the rate of heating and the amount of oxidation that may occur. If the metal is heated relatively slowly (about 0.3°C per second) in the presence of water and/or air, as noted above, the molten metal and its oxide film is expected to "bloat"^(3,4) and block passages. In the most severe case, the metal will be restrained from flowing to the bottom of the core when the melting point of the SS is reached. If sufficient water and/or air can reach this metal froth, the oxidation will continue. At equilibrium conditions, the

oxidized metal will contain some of the following: FeO , Fe_3O_4 , Fe_2O_3 , CrO_3 , Cr_2O_3 , NiO , and mixed spinels. These oxides probably will react with the UO_2 and UO_{2+x} to form lower melting phases. Since the phase equilibria for these oxides with UO_2 have not been determined, the lowest temperature of liquid formation is unknown. (See discussion under MP of UO_2 -SS oxides.) It is notable, however, that if the melting metal "bloats" and blocks the fuel passages, the oxidation probably will cease and the SS oxide- UO_2 reactions will be of little significance. In the case of more rapid heating of the SS-clad UO_2 (about 3°C per second) the molten metal is expected to flow down without much reaction with the UO_2 .

V. GENERAL CONSIDERATION OF IRRADIATION EFFECTS AND U BURNUP

When a loss-of-coolant incident occurs, the fuel elements will have suffered a degree of material damage and alteration dependent on the amount of U atom burnup. These effects will be measurable as material property changes arising from crystalline lattice damage during irradiation and as fission products from the fissioning of the U atoms.

The most noticeable effects of irradiation will be lowering of the thermal conductivity of all materials and a decrease in the ductility of the cladding metal. Since these effects are inherently dependent on crystalline lattice distortions, thermal treatment as the excursion progresses tends to reduce the effect of irradiation on the physical and mechanical properties. Thus, if the temperature rises at a relatively slow rate, some of the radiation-induced physical property damage will be annealed. The most pronounced effect(s) will probably be the higher radial temperature gradient(s) in the fuel element because of the lowered thermal conductivity. A second possible effect resulting from the embrittlement of the cladding, may be early rupture (splitting or transverse cracking) of the cladding if there is a substantial build-up of cladding stress during the temperature rise.

The most pronounced effect of the fission products from the fuel fissioning at high temperature is fission gas release. This effect will be dependent on the rate of heating and the details of the fuel element. Thus, if the temperature rise is rapid and the fission product gaseous species cannot

escape from the element, the element may deform or rupture from the pressure build-up as the temperature increases.

The irradiation is not expected to have any significant effect on the rate of oxidation of the metal cladding. Likewise, low burnup (< 1000 MWD/MT) is not expected to show any significant effect on the other anticipated reactions.

VI. SUMMARY

Available high-temperature physical and mechanical data on materials pertinent to a loss-of-coolant incident involving Zircaloy-clad or Type-304-SS-clad UO_2 fuel elements have been summarized and, where appropriate and necessary, the values discussed in detail. The most obvious gaps in information occur in the high-temperature region for physical and mechanical properties of the UO_2 and the cladding materials. The specific data needed are outlined below:

A. Physical Property Data:

- (1) Thermal expansion of UO_2 in the temperature range from 2250° to 2800°C .
- (2) Thermal expansion of Zircaloy-4 to 1800°C .
- (3) Total emittance of UO_2 .
- (4) Thermal conductivity of 304 SS in the temperature range from $\sim 700^\circ$ to $\leq 1400^\circ\text{C}$.
- (5) Emittance of Zircaloy-4 as it oxidizes.

B. Mechanical Property Data Needed:

- (1) Ductility and strength of irradiated Zircaloy-4 tubing as a function of heating rate and stress.
- (2) Ductility and strength of irradiated 304 SS tubing as a function of heating rate and stress.
- (3) Effect of oxidation on the embrittlement of Zircaloy-4.

While there are many additional areas where measurements must be made to complete the high-temperature property data, the need for this information must be clarified. That is, in view of the complex situation in meltdown, one must decide how much additional refinement of the existing data is of value for pre-analysis model calculations, and what properties are pertinent based on the observed behavior of the clad UO_2 as it undergoes a meltdown similar to that anticipated in a loss-of-coolant incident.

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Fig. 1 - Melting points of uranium dioxide^(11,12) versus O/U ratio

Fig. 2 - Enthalpy - temperature data for uranium dioxide (16)

Fig. 3 – Zirconium-oxygen system^(5,6)

Fig. 4 - Proposed zirconia-rich portion of system $ZrO(23)$

Fig. 5 - Thermal expansion of UO_2 (26)

Fig. 6 — Thermal expansion of monoclinic ZrO_2 (84)

Fig. 7 — Total emissivity of Zircaloy 2 versus oxygen addition for a surface oxide at temperatures between 775° and 875°C(29)

Fig. 8 - Total emittance of zirconia (28,35)

Fig. 9 – Thermal conductivity versus temperature for Zircaloy-4^(37,36,38)

Fig. 10 – Thermal conductivity of 304 SS^(39,41)

Fig. 11 — Relationship between thermal conductivity and oxygen content for UO_{2+x} at 920°C (50)

Thermal conductivity, watts/cm-°C)

Fig. 12 — The thermal conductivity as a function of temperature for unirradiated uranium oxides of different compositions. (51)

Fig. 13 — UO_2 thermal conductivity versus temperature for 95 percent theoretical density (43)

Thermal conductivity (watts/cm-°C)

0.042

0.038

0.034

0.030

0.026

0.022

0.018

0.014

900

1100

1300

1500

1700

1900

2100

2300

Mean temperature, °C

$\text{ZrO}_2 (\text{Y}_2\text{O}_3)$
(54)

$\text{ZrO}_2 (\text{Y}_2\text{O}_3, \text{Zr})$
(47)

$\text{ZrO}_2 (\text{CaO})$
(47), (53)

Fig. 14 — Thermal conductivity as a function of temperature for stabilized ZrO_2

Fig. 15 - Enthalpy - temperature data for stoichiometric UO_2 ⁽¹⁶⁾

Tensile strength, kg/mm²

Fig. 16 — Ultimate tensile strength of Zr-4

Fig. 17 — Tensile strength of 304L stainless steel as a function of temperature

Fig. 18 – Ductility versus temperature for Zircaloy-4 sheet based on tensile tests in argon³⁰

Fig. 19 – Ductility of 304L stainless steel

Fig. 20 – Oxidation of Zr by steam⁷⁵

Fig. 21 — Parabolic rate constants for Type 304 stainless steel — steam reaction versus reciprocal absolute temperature⁷⁵

Fig. 22 — $\text{UO}_2\text{-ZrO}_2$ phase diagram (9)

TABLE I
HIGH TEMPERATURE PHYSICAL PROPERTIES OF SELECTED FUEL ELEMENT MATERIALS

	Zirconium	Zircaloy-4	Type 304 SS	UO ₂	ZrO ₂
1. Melting Point, °C	1852 ± 10 (79)	1849 (7)	1400-1455 (25)	2840 (See discussion and Figure 1) (11, 12)	2710 ± 15 (83)
2. Boiling Point, °C	4325 (80)	---	Cr 2567 Fe 2772 Ni 2142 (80)	---	4297 (81)
3. Heat of Fusion ΔH _M , kcal/mole	4.9 (79)	---	Cr 3.5 Fe 3.7 Ni 4.21 (79)	18.2 ± 0.5 (See Figure 2) (16)	20.8 (81)
4. Heat of Vaporization, ΔH _V , kcal/mole	145.76 ± 1.0 (79)	---	Cr 94.85 Fe 99.95 Ni 102.67 (79)	137.1 ± 1.7 (1800°K) (82)	157.3 - 0.0078T - 400/T (20)
5. Vapor Pressure Above Solid, in Torr at T°K	$\log P = 10.216 - \frac{31,066}{T} - 0.0002419T$ (80)	---	Cr) $\log P = 7.127 - \frac{20059}{T}$ Fe) $\log P = 7.023 - \frac{20826}{T}$ Ni) $\log P = 7.341 - \frac{21911}{T}$ (79)	$\log P = 25.686 - 33,115/T - 4.026 \log T$ (82)	$\log P = \frac{-35,900 \pm 1000}{T} + (10.77 \pm .39)$ (20)
6. Phase Transformation	α → β (870°C) β = Cubic (2285°C) See Discussion and Figures 3 and 4 (79)	α → β (900 - 1000°C) (7)	---	None	Monoclinic → Tetragonal (1100-1250°C) Tetragonal → Cubic (2250°C) (9)
7. Coefficient of Thermal Expansion at t°C; given as °C ⁻¹	$(5.768 + 0.006154t) \times 10^{-6}$ for α 9.7×10^{-6} for β	$5.63 \times 10^{-6} + 3.16 \times 10^{-9}t$ (25-800°C only) (24)	Mean coefficient = 2.02×10^{-5} (0 - 1000°C) (25)	$6.797 \times 10^{-6} + 5.792 \times 10^{-9}t$ (1000 - 2250°C) See Figure 5 (26)	Mean coefficient = 7.8×10^{-6} (0 - 1000°C) See Figure 6 (84)
8. Density, g/cc, 25°C	6.49 (25)	---	7.9 (25)	10.96 (8)	5.68 (85)
9. Total Normal Emittance at t°C	0.118 + 0.000127t (15)	0.112 + 0.000085t (37)	0.707 + 0.000232t based on Ref. 33; 300 - 800°C	---	See Figure 8 (28)
10. Thermal Conductivity Watts/cm ² °C	0.211 at 25°C 0.204 at 100°C 0.187 at 300°C (25)	(25 - 1500°C) See Figure 9 (36-38)	(100 - 740°C data only) See Figure 10 (39, 41)	See Figures 11-13 (43-51)	See Figure 14 (47)

Continued on next page

TABLE I (Continued)

II. Enthalpy ($H_T - H_{298}$) in cal/g mole or cal/g atom and heat capacity (C_p) in cal/g mole-°C or cal/g atom-°C; T in °K.

Material	Phase	Temp. Range, °K	$H_T - H_{298}^{\circ}$	C_p
Zr (79)	α	298-1143	$-1868 + 5.661T + 1.075 \times 10^{-3}T^2 + 25685/T$	$5.661 + 0.00219T - 25685/T^2$
	β	1143-2125	$468 + 4.859T + 0.803 \times 10^{-3}T^2$	$4.859 + 0.001606T$
Zircaloy-2 (22)	α	273-908	$-1777 + 5.64T + 1.094 \times 10^{-3}T^2$	$5.64 + 2.187 \times 10^{-3}T$
	α	908-1083	$-2910.6 + 7.870T$	7.870
	β	1248-1325	$-1888 + 7.833T$	7.833
Type 304 SS (79,81)	Calculated from individual component data			
Fe	α	298-1033	$-1176 + 3.37T + 3.55 \times 10^{-3}T^2 - 0.43 \times 10^5/T$	$3.37 + 7.10 \times 10^{-3}T + 0.43 \times 10^5/T^2$
	δ	1033-1184	$-4280 + 10.40T$	10.40
	γ	1184-1665	$-325 + 6.36T + 7.5 \times 10^{-4}T^2$	$6.36 + 1.5 \times 10^{-3}T$
	δ	1665-1809	$-1154 + 6.76T + 9 \times 10^{-4}T^2$	$6.76 + 1.8 \times 10^{-3}T$
	liq.	1809-3500	$-698 + 9.78T + 2 \times 10^{-4}T^2$ (est.)	$9.78 + 4 \times 10^{-4}T$ (est.)
Cr		-2176	$-1567 + 4.73T + 1.535 \times 10^{-3}T^2 + 622/T$	$4.73 + 3.07 \times 10^{-3}T - 622/T^2$
	liq.	2176-	$570 + 9.4T$	9.4
Ni		700-1725	$-7210 + 5.68T + 0.001T^2 - 142100/T$	$5.68 + 0.002T + 142100/T^2$
	liq.	1725-	$-300 + 9.2T$	9.2
UO ₂ (81) (79)		298-1500	$-7125 + 19.20T + 0.81 \times 10^{-3}T^2 + 3.96 \times 10^5/T$	$19.20 + 1.62 \times 10^{-3}T - 3.96 \times 10^5/T^2$
		1170-3115	$-7667 + 20.52T + 1.468 \times 10^{-4}T^2 + 41870E/(1+E)$ where $E = \exp(6.16 - 41870/RT)$	$20.52 + 0.000294T + [41870/(1+E)T]^2 E/R$
(Figure 2) (16)	liq.	3115-3260	$-12911 + 33.096T$	33.1
ZnO ₂ (81)	α	298-1478	$-6160 + 16.64T + 0.90 \times 10^{-3}T^2 + 3.36 \times 10^5/T$	$16.64 + 1.80 \times 10^{-3}T - 3.36 \times 10^5/T^2$
	β	1478-2100	$-4267 + 17.80T$	17.80

TABLE II
SELECTED HIGH TEMPERATURE MECHANICAL PROPERTIES OF FUEL ELEMENT MATERIAL

	Zircaloy	304 SS	UO ₂	ZrO ₂ (MgO Stab.)
1. Tensile Strength	See Figure 16 (30,37)	See Figure 17 (67)	$S = 287.56G^{-0.837}e^{-5.84p}$ Where S is in kg/mm ² G is grain size, μ p is fraction porosity (88)	Temp. °C kg/mm ² 1030 9.30 1200 8.42 1540 1.3 (90)
2. Compressive Strength				Temp. °C kg/mm ² 1000 120 1200 80 1400 13 1500 2 (90)
3. Ductility (Elongation)	See Figure 18 (30)	See Figure 19 (67)		
4. Modulus of Elasticity, kg/mm ²	9841-5.78t (°C) to 320°C (86)	21,840 - 9.326t (°C) to 1000°C (87)	16,900 kg/mm ² at 800°C (93% of theoretical density) (89)	Temp. °C kg/mm ² 1050 11,600 1180 11,100 1225 10,700 1290 10,300 1360 9,600 (90)