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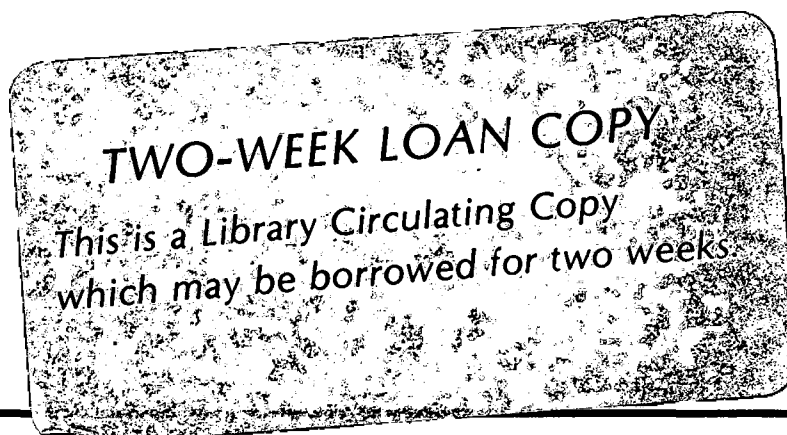
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DOCUMENTS SECTION

**INTERACTION OF URANIUM DIOXIDE
WITH MOLTEN ZIRCALOY**

K.T. Kim
(Ph.D. Thesis)

April 1987



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INTERACTION OF URANIUM DIOXIDE WITH MOLTEN ZIRCALOY

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April 1987

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Berkeley Laboratory and the Department of Nuclear Engineering of
the University of California, Berkeley, California 94720

ABSTRACT

Laboratory experiments in which gram quantities of molten Zircaloy were held in contact with UO_2 for known times (20 - 600 s) and temperatures (1900 - 2200°C) were conducted. Following each experiment, polished sections of the specimen were examined by optical microscopy, electron microprobe, scanning Auger microscopy and X-ray fluorescence spectroscopy.

Three closely-related experiments were conducted. In the first, the molten metal was contained in a UO_2 crucible. The dissolution rate in this system was found to be dominated by natural convection in the melt driven by density gradients established by the dissolving uranium. The mechanism of the interaction also was observed to involve penetration and detachment of the grains of the oxide by the molten metal. Similar tests with single-crystal UO_2 specimens showed similar dissolution behaviour. Less severe attack occurred because of the absence of grain boundaries, although subgrain boundaries or dislocations provided high-diffusivity pathways for preferential oxygen removal.

In the third type of test, a disk of UO_2 was placed at the bottom of a ThO_2 crucible. This arrangement prevented establishment of unstable density gradients in the liquid phase, resulting in a purely diffusion-controlled interaction. A remarkable seven-region structure was observed in the quenched specimens. This structure could be explained by analysis of

the quenching of the high-temperature interaction zone with the aid of the available ternary phase diagrams of the U-Zr-O system. The layers grew parabolically in time.

The relevance of the data obtained to the melting on fuel pellets in a severe fuel damage accident was assessed.

ACKNOWLEDGMENTS

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1. INTRODUCTION

1.1 Objective

In the TMI accident, the reactor core temperature exceeded the melting point of Zircaloy (1760 °C). In out-of-pile integral rod and bundle tests at KfK(1), it has been shown that cladding temperatures can increase up to 2200 °C by the exothermic oxidation process and that solid UO_2 can be partially dissolved by the molten cladding. Any dissolution of UO_2 by the molten cladding, or any structural changes occurring in the UO_2 , may result in increased fission-product release from the fuel. Furthermore, extensive UO_2 /solid Zircaloy out-of-pile experiments(2) have shown that Zircaloy cladding can be oxidized by UO_2 fuel as quickly as by steam. It is, therefore, important to understand the reaction phenomena of the UO_2 /Zircaloy system at temperatures below and above the melting point of Zircaloy.

In order to understand clearly the UO_2 /Zircaloy interaction, reliable phase diagrams of the U-Zr-O system and kinetic data on the UO_2 /Zircaloy system are required. Partial phase diagrams of the U-Zr-O system at various isothermal sections have been proposed by several investigators(3,4,5). There are, however, some discrepancies between them. On the other hand, the kinetics of the interaction between UO_2 and both solid and liquid Zircaloy has been extensively studied by several investigators(2,6,7,8,9). There is quite good agreement in the kinetic data, reaction products, and layer sequences of the UO_2 /solid Zircaloy reaction. For the UO_2 /liquid Zircaloy, however, there has been insufficient information reported up to now.

The laboratory experiments described here were performed in the temperature range 1900 to 2200 °C under inert gas conditions to study the interaction between UO_2 and liquid Zircaloy.

The general objectives of the present work were

- to identify the reaction products and layers,
- to determine the mechanism of UO_2 dissolution by molten Zircaloy.
- to determine the saturation concentration of uranium in the Zry melt,
- to investigate the structural changes in the undissolved UO_2 resulting from the interaction,
- to determine the diffusion path in the U-Zr-O phase diagram,
- to develop the laws governing the layer growth rates,
- to develop the laws governing the dissolution rate of UO_2 ,

1.2 Review of the Zircaloy- UO_2 Reaction : Previous Work

1.2.1 The U-Zr-O Phase Diagrams

Since Saller et al(10) proposed isothermal sections of the U-Zr-O phase diagram up to 1100 °C, Politis(3) obtained isothermal sections at 1000, 1500, and 2000 °C and a quasi-binary section between $\alpha\text{-Zr(O)}$ ¹ and UO_2 . These are shown in Fig. 1.1 and 1.2, respectively. Yamanaka et al (5) reported the isothermal section at 1000 °C which is qualitatively in good agreement with the phase diagram reported by Politis(3). However, the location of the boundary between the three-phase region of [$\text{UO}_2 + \alpha\text{-Zr(O)} + (\text{U,Zr})$] and the two-phase region of [$(\text{U,Zr}) + \alpha\text{-Zr(O)}$] differs slightly from that of Politis.

Recently Skokan(4) proposed isothermal sections at 1600, 1800, 1905 and 1950 °C (Fig. 1.1) and quasi-binary section between UO_2 and $\alpha\text{-Zr(O)}$ (Fig. 1.2). According to his data, the temperature of the eutectic is 60 °C higher than the earlier data (1840 °C) (3) and the eutectic point in the quasi-binary system does not lie at 5 mol % UO_2 as determined ear-

[1] $\alpha\text{-Zr(O)}$ designates the alpha phase of zirconium (or Zircaloy) containing high(~ 30 a/o or ~ 6.9 w/o) concentration of dissolved oxygen.

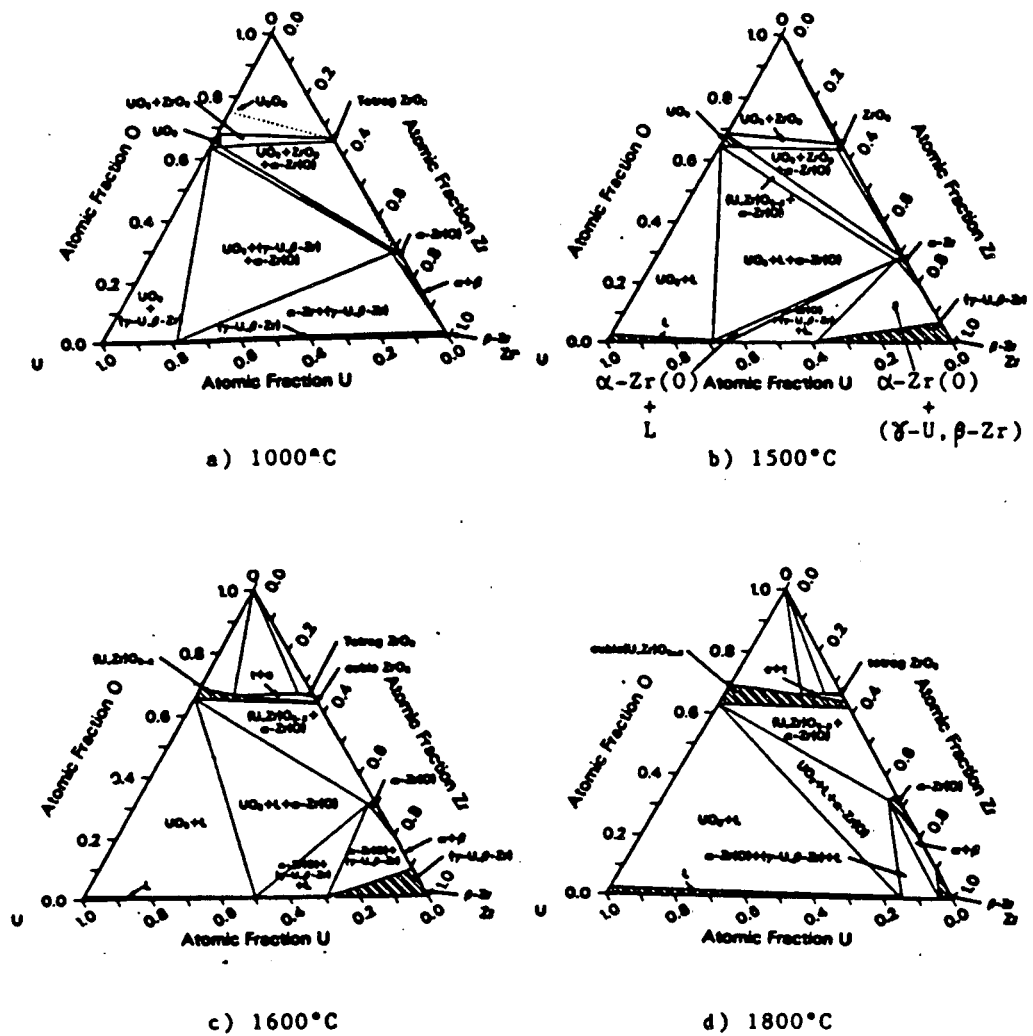
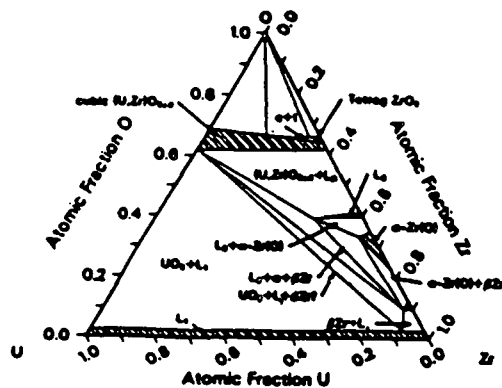
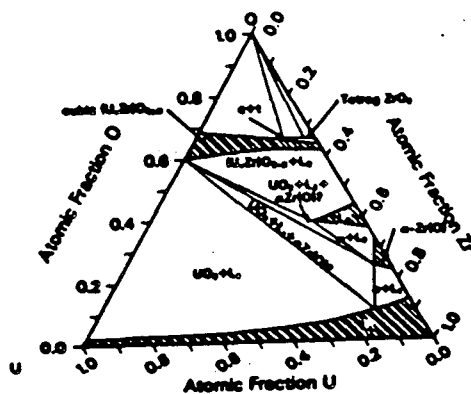


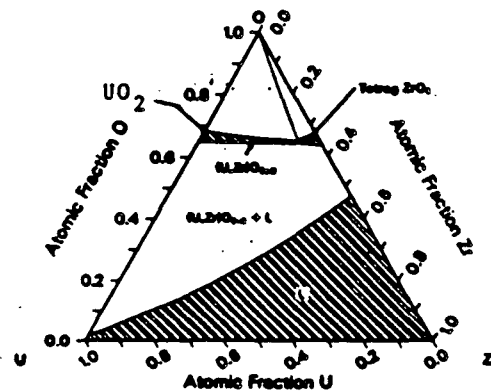
Fig. 1.1 Equilibrium Phase Diagrams of the U-Zr-O System(3,4).



e) 1905°C



f) 1950°C



g) 2000°C

Fig. 1.1 (Continued)

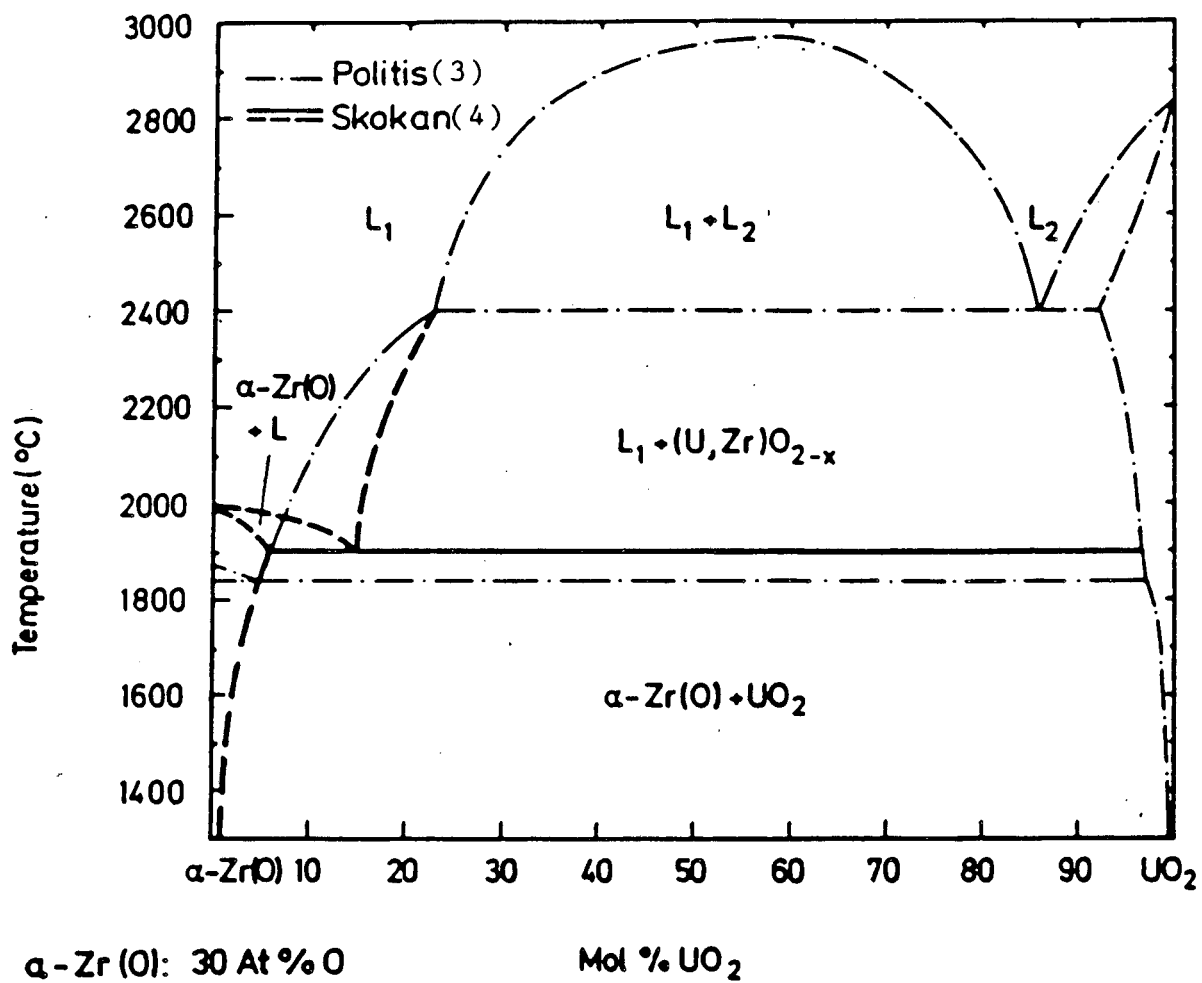


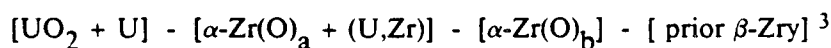
Fig. 1.2 Quasi-binary $\alpha\text{-Zr(O)} / UO_2$ Phase Diagram.

lier(3), but at 15 mol % UO_2 . The revised quasi-binary phase diagram, therefore, eliminated a noticeable inconsistency between the earlier quasi-binary sections and the ternary isothermal sections, concerning the liquidus curve of the two-phase region of $[(\text{U,Zr})\text{O}_{2-x} + \text{L}]$ at the Zr-rich side. This is discussed in detail in Appendix G. There are, however, still some inconsistencies in drawing the solidus curve of the two-phase region of $[(\text{U,Zr})\text{O}_{2-x} + \text{L}]$ in the ternary isothermal section at 2000 °C(3). The quasi-binary section(Fig 1.2) shows that the solubility of Zr in $(\text{U,Zr})\text{O}_{2-x}$ increases with an increase of temperature. Comparison of the ternary isothermal section at 1950 °C with that at 2000 °C(Fig. 1.1) shows the opposite trend.

1.2.2 Corrosion Kinetics of the UO_2 -Solid Zry Couples

The reaction of UO_2 with Zr and Zry² was studied by Mallet et al (11) at temperatures up to 1200 °C for long reaction times. Yet the extrapolation of his results to higher temperatures and shorter reaction times has limited validity.

More recently, the reaction kinetics were reported by Hofmann et al(2), who performed extensive UO_2 /Zry out-of-pile experiments between 1000 to 1700 °C in an inert atmosphere with external overpressure. The reaction layers formed the following sequence at all reaction temperatures and times :



These are shown schematically in Fig. 1.3. The $\alpha\text{-Zr(O)}_b$ zone contains no (U,Zr) alloy and uranium, in contrast to the $\alpha\text{-Zr(O)}_a$ zone, which is a two-phase. In the temperature range examined, the rates of growth of the three central layers obey parabolic rate law and the diffusion of oxygen in Zr is the rate-controlling step in the reaction. Furthermore, it has

[2] Zry is an abbreviation of the commercial alloy Zircaloy which contains 98.5 % Zr, 1.5 % Sn and small quantities of Fe, Cr and Ni (Table 1).

[3] During the experiment, this portion was β -phase, and transformed into α -phase during cooling-down. At room temperature, it is referred to as prior β -Zry.

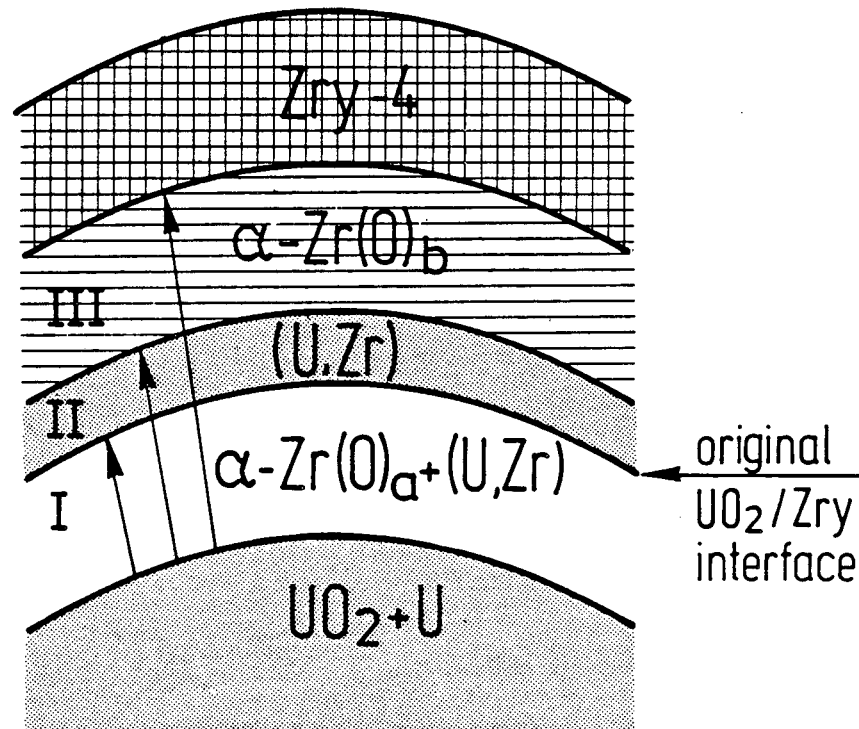


Fig. 1.3 Schematic representation of the UO₂/Zircaloy-4 reaction zones. The (U,Zr) alloy is located between two $\alpha\text{-Zr(O)}$ phases. The $\alpha\text{-Zr(O)}_a$ phase, in contrast to the $\alpha\text{-Zr(O)}_b$ phase, contains uranium particles. Ref. 2.

been shown that Zircaloy cladding can be oxidized by UO_2 as quickly as by steam.

Yamanaka(5) and Hutchings(6) reported limited out-of-pile UO_2/Zry reaction data, which confirmed the results of Hofmann et al. Several theoretical analyses(12,13), using the results of Hofmann et al(2), have been performed in an attempt to elucidate the mechanism of formation of the three layers.

1.2.3 Corrosion Products in the UO_2 -Liquid Zry Couples

Rosinger et al (6) reported that, in an inert atmosphere, UO_2 and molten Zry interact to form $[\alpha\text{-Zr(O)} + (\text{U,Zr})]$ and a homogeneous liquid (U,Zr,O) alloy at temperatures from 1760 to 1970 °C. At temperatures above 1970° C, the melting point of oxygen stabilized $\alpha\text{-Zr(O)}$, there exists only a homogeneous liquid (U,Zr,O) phase.

Hofmann et al(8) showed that molten Zry reduces UO_2 by forming a homogeneous (U,Zr,O) melt. If a certain amount of oxygen content in the (U,Zr,O) melt is exceeded, solid $(\text{U,Zr})\text{O}_{2-x}$ particles tend to precipitate at annealing temperatures from 1800 to 2000 °C. In addition, they argued that the amount of fuel which can be liquefied by molten cladding depends on the initial oxygen concentration of the melt. The higher the initial oxygen concentration of the melt, the smaller the amount of fuel which can be dissolved. They also reported that the interaction of UO_2 and molten Zry resulted in a sudden disintegration of the solid UO_2 and argued that this phenomenon is probably due to liquid uranium which forms preferentially along the UO_2 grain boundaries near the UO_2/Zry interface.

According to Fig. 1.1, the system at 2000° C contains only two phases, the (U,Zr,O) liquid and the mixed hypostoichiometric solid oxide $(\text{U,Zr})\text{O}_{2-x}$. It is generally believed that during cooling-down the liquid (U,Zr,O) alloy phase decomposes to form two metallic phases, $\alpha\text{-Zr(O)}$ and (U,Zr) , at low oxygen content, and to form the two metallic phases and one ceramic phase, $(\text{U,Zr})\text{O}_2$, at high oxygen content. The solid $(\text{U,Zr})\text{O}_{2-x}$ phase also decomposes to form $(\text{U,Zr})\text{O}_2$ and (U,Zr) . The $(\text{U,Zr})\text{O}_2$ decomposition product remains a

non-equilibrium phase at room temperature rather than decomposing to form UO_2 and ZrO_2 , as the phase diagram at 1500 °C (see Fig. 1.1) would suggest.

Hagen et al(1) performed out-of-pile integral rod and bundle tests up to 2200 °C in steam atmosphere to investigate UO_2 dissolution by molten Zry. They observed three phases, $(\text{U,Zr})\text{O}_2$, $\alpha\text{-Zr(O)}$ and (U,Zr) at room temperature, which they assumed to have arisen from a homogeneous (U,Zr,O) phase at the test temperature.

1.2.4. Effects of Convection in the UO_2 -Liquid Zry Interaction

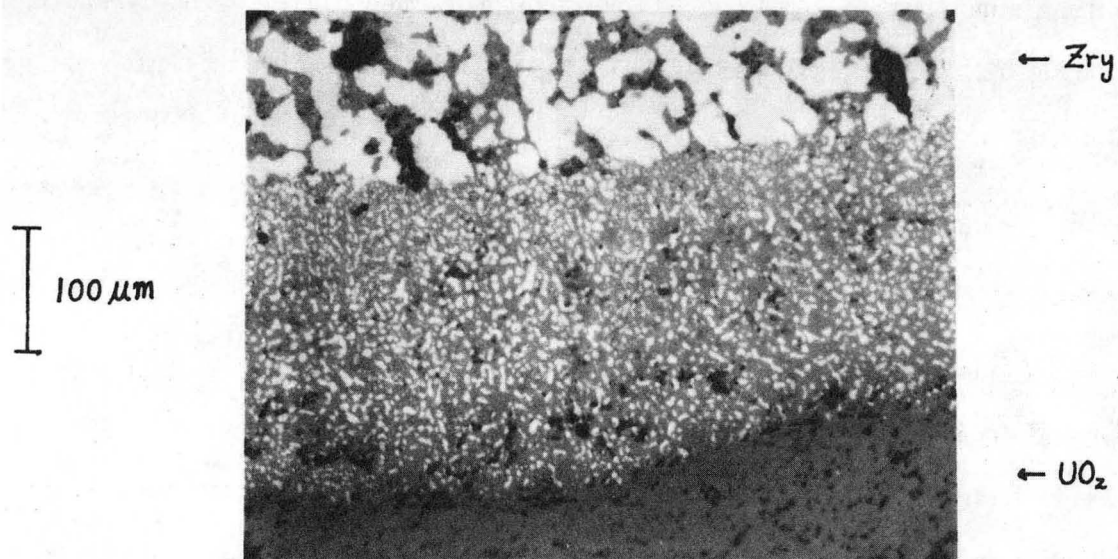
Examining closely the results reported and experimental designs of the previous UO_2 -liquid Zry interaction(1,6,8), there appears to be no concentration gradient in the liquid Zry zone, regardless of reaction time. It is, therefore, believed that there exists a significant bulk motion of the liquid Zry caused by natural convection. This convection is driven by buoyancy forces produced by the density differences between the reaction products[e.g., liquid (U,Zr,O)] and the molten Zry during isothermal reaction, and by the temperature gradient in the liquid phase during cooling-down. It is, therefore, impossible to determine the reaction kinetics between UO_2 and liquid Zry without considering the effects of convection on the reaction. From the ternary phase diagram at 2000 °C (Fig. 1.1), there should be a two-phase zone $[(\text{U,Zr})\text{O}_{2-x}$ and $(\text{U,Zr,O})]$ at the metal/ceramic interface. However, if there is a significant convection, $(\text{U,Zr})\text{O}_{2-x}$ particles in this two-phase zone can be swept away from the reaction interface and be dissolved in oxygen-poor bulk liquid Zry. On the other hand, even in the presence of convection, it is likely that some of the two-phase interaction zone will remain attached to the still-solid fuel. This is shown in Fig. 1.4, which is taken from Hagen's work(1), in which strong gravity-driven vertical flow of the melt occurred.

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Chemical attack of solid UO_2 by molten Zry-2
($T \approx 2000^\circ\text{C}$, $t = 300 \text{ sec}$, $\times 200$)

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Fig. 1.4

1.3 Review of Natural Convection in an Enclosure

In order to provide a general idea of natural convection in the UO_2 crucible, flow behaviour and basic fluid-mechanical parameters describing natural convection are discussed in this section.

Natural convection constrained in an enclosure is encountered in many engineering applications, including the storage of cryogenic fluids, petroleum storage vessels and the storage of hot fluids for solar power plants. Extensive analytical and experimental work(14-19) has been conducted with fluids in such enclosures subject to the restraint of constant heat flux. The previous experimental studies(14,17) provided gross ideas of the flow behaviour, as shown in Fig. 1.5. This figure shows three regions : a boundary layer rising at the heated wall, a mixing region at the top, and a central main core. The heated fluid in the vicinity of the wall rises up the boundary layer to the mixing region. Here, it flows toward the center of the vessel, disperses and mixes, and returns as a downward motion of the heated fluid. However, if the enclosure is cooled at the wall, the flow direction is reversed. The axial velocity distribution in the boundary layer starts at zero at the wall, rapidly grows to its maximum value, and slowly returns to zero at a position, which defines the thickness of the boundary layer, δ . The main core, however, is characterized by plug velocity. These processes of natural-convective flow and mixing are extremely complex and presently not well understood. On the other hand, Barakat and Clark(18) calculated the stream lines for circulation in a liquid with no lid, as shown in Fig. 1.6. This figure shows that the heated fluid in the vicinity of the wall rises until it approaches the liquid surface, where it smoothly changes its direction to downward flow.

It is convenient to consider which dimensionless variables influence the flow and heat transfer under natural convection. By writing the appropriate continuity, momentum, and energy equations in terms of the dimensionless variables, it is seen that, for thermally-driven natural convection, the two dimensionless groups, the Prandtl number ⁴ and the Grashof

[4] Prandtl number(Pr) is defined as $\left[\frac{\nu}{\alpha} \right]$ in which ν represents kinematic viscosity and α thermal

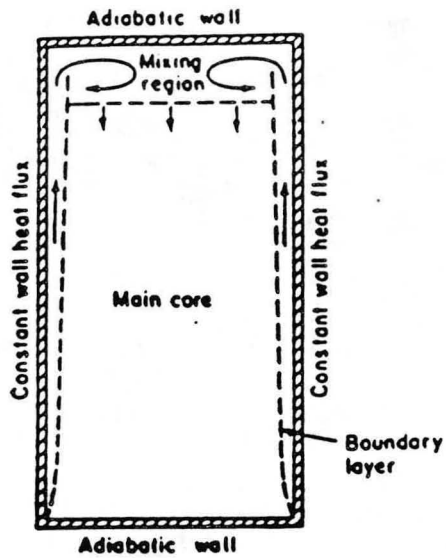


Fig.1.5 Model for Natural Convection within a Vertical Cylinder for Constant Wall Heat Flux.

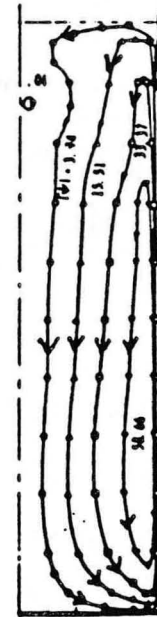


Fig.1.6 Streamlines for Natural Convection within a Vertical Cylinder for Constant Wall Heat Flux.

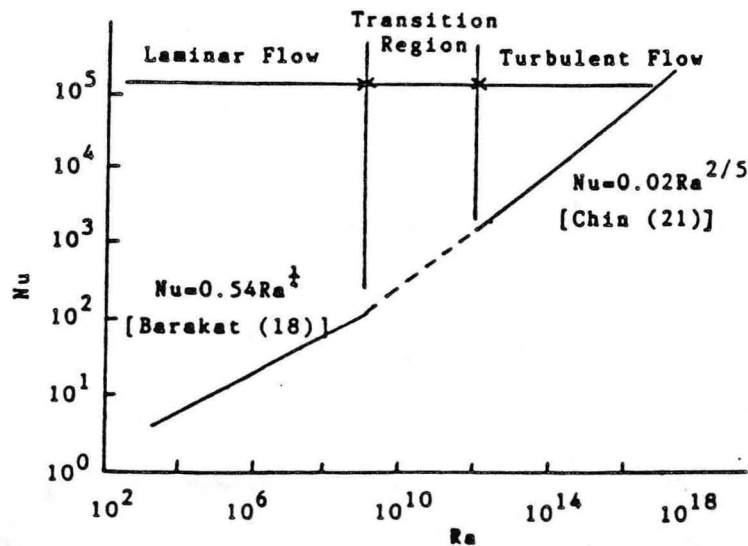


Fig.1.7 Natural Convection Correlations

number⁵ appear in the the three conservation equations(20). The nature of a natural convection boundary layer flow can be described by the magnitude of the Raleigh number Ra , which is the product of the Grashof number Gr and the Prandtl number Pr :

$$Ra = \left[\frac{g\beta\Delta T d^3}{\nu^2} \right] \left[\frac{C_p \mu}{k} \right] \quad (1.1)$$

for the case of a uniform wall temperature, or by the modified Raleigh number Ra^* :

$$Ra^* = \left[\frac{g\beta q_w d^4}{k \nu^2} \right] \left[\frac{C_p \mu}{k} \right] \quad (1.2)$$

for constant heat flux(q_w). Complete viscous flow can be expected if $Ra^* \leq 10^4$. Transition from laminar to turbulent flow occurs when Ra is approximately 10^9 or when Ra^* is approximately 10^{11} .

Barakat et al(18) and Chin et al(21) provided the correlations of the Nusselt number versus the Raleigh number for thermally-driven natural convection(Fig. 1.7). For laminar flow, the Nusselt number is expressed by the following relationship :

$$\frac{Nu}{Ra^{\frac{1}{4}}} = B \quad (1.3)$$

Barakat et al(18) recommend a value of $B=0.54$. In addition, Hess and Miller(19) reported that the maximum velocity inside the boundary layer is closely related to the Raleigh number by the following expression :

$$\frac{v_{m1}}{v_{m2}} = \left[\frac{Ra_1}{Ra_2} \right]^{\frac{1}{4}} \quad (1.4)$$

where subscripts 1 and 2 correspond to two different cases. They also reported that the boundary layer thickness δ is closely related to the Raleigh number by the following expression :

$$\frac{\delta_1}{\delta_2} = \left[\frac{Ra_2}{Ra_1} \right]^{\frac{1}{4}} \quad (1.5)$$

diffusivity.

[5] Grashof number(Gr) is defined as $\left[\frac{\beta g \Delta T d^3}{\nu^2} \right]$ in which β represents thermal expansion coefficient and d characteristic length.

where subscripts 1 and 2 correspond to two different cases. These two relationships indicate that, as the Raleigh number increases, the maximum velocity increases and the boundary layer thickness decreases. This means that larger value of Ra(e.g., a larger temperature difference or a smaller viscosity) gives faster mixing.

It is well-known that the differential equations for heat transfer and mass transfer are analogous if chemical reactions in fluid can be neglected. In order to obtain concentration profiles instead of temperature profiles, however, one simply replaces the Prandtl number by the Schmidt number $[Sc = \frac{\nu}{D}]$ and changes T to X_A , where D = mutual diffusivity and X_A = molar fraction of A component. Then, the Nusselt number for the concentration difference-driven natural convection system will be described by the following expression :

$$\frac{Nu_{AB}}{Ra_{AB}^{\frac{1}{4}}} = B \quad (1.6)$$

Note that, for the concentration difference-driven natural convection, the Nusselt number and the Raleigh number are defined by the following expressions :

$$Nu_{AB} = \frac{k_x d}{D} \quad (1.7)$$

$$Ra_{AB} = Gr_{AB} Sc = \left[\frac{\zeta g \Delta x_A d^3}{\nu^2} \right] \left[\frac{\nu}{D} \right] \quad (1.8)$$

in which k_x = the mass transfer coefficient, d = the diameter of enclosure and $\zeta = \frac{-1}{\rho} \left(\frac{\partial \rho}{\partial X_A} \right)_{P,T}$

Furthermore, $\zeta \Delta x_A$ can be approximated as $\frac{\Delta \rho}{\rho_m}$, in which $\Delta \rho$ = density difference between the liquid in contact with the wall of a crucible and the liquid in the bulk region, and ρ_m = average density of the liquid. Then, Eq. (1.8) is modified as :

$$Ra_{AB} = \left[\frac{\Delta \rho}{\rho_m} \right] \left[\frac{g d^3}{\nu^2} \right] \left[\frac{\nu}{D} \right] \quad (1.9)$$

The above considerations will be used in Appendix D to calculate uranium transport by natural convection.

2. EXPERIMENTAL

2.1 Materials

2.1.1 Zircaloy

Zry-2 and Zry-4 used in the present work were supplied by the Wah-Chang Company. Typical compositions of Zry-2 and Zry-4 are given in Table 1. Note the low oxygen content of the as-received Zry(0.8 a/o). The UO_2/Zry reaction experiments performed at temperature range from 1900 and 2200 °C showed no distinguishable difference between Zry-2 and Zry-4.

In order to investigate the effects of the initial oxygen content of the Zry on the UO_2/Zry reactions, the as-received Zry was machined to a solid cylindrical shape and charged with oxygen. An oxide coating of the desired thickness was applied to the specimens by heating in a furnace containing oxygen at 850 °C for 2 and 9 hrs to attain the intended oxygen contents of 2.4 and 5.0 w/o, respectively, within $\pm 2\%$. The weight increase of the Zry specimen was used as a monitor to determine the amount of oxygen added to the Zry. Homogenization was accomplished in an induction furnace under Ar - 5 % H_2 atmosphere at 1500 °C for 3 hrs. During this treatment, weight increases up to 0.2 % were observed. The oxidized and the homogenized specimens are shown in Fig. 2.1. This figure shows that the ZrO_2 layer was transformed to $\alpha\text{-Zr(O)}$ layer after homogenization.

2.1.2 UO_2

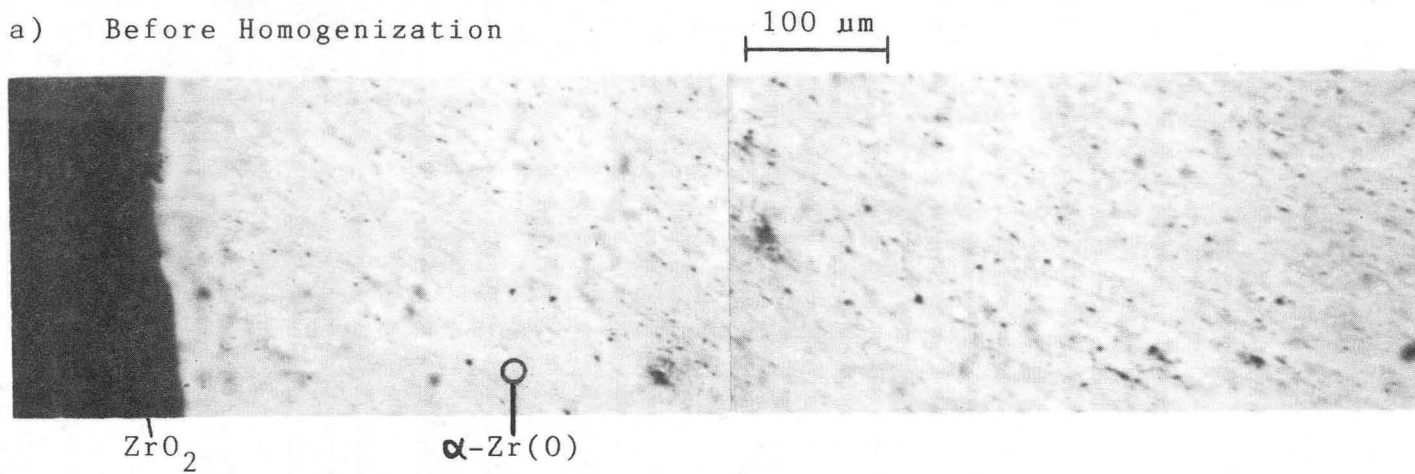
In this work, UO_2 single crystals and polycrystalline UO_2 samples were used. UO_2 single crystal spheres 3 mm in diameter were supplied by the Hanford Laboratories and polycrystalline UO_2 pellets by the General Electric Company. These pellets were machined in disks or crucibles with a closed bottom.

Table 1. Compositions of Zry-2 and Zry-4*

Alloying element (wt %)	Zry-2	Zry-4
Sn	1.50 (1.20 - 1.70)	1.50 (1.20 - 1.70)
Fe	0.12 (0.07 - 0.20)	0.20 (0.18 - 0.24)
Cr	0.10 (0.05 - 0.15)	0.10 (0.07 - 0.13)
Ni	0.05 (0.03 - 0.08)	0.007
total Fe,Cr,Ni	(0.18 - 0.38)	0.28
O (ppm)	1000 - 1400	1000 - 1400

* Data from S. Kass, "Corrosion of Zirconium Alloy," ASTM Special Technical Publication No.368, 1963

a) Before Homogenization



b) After Homogenization

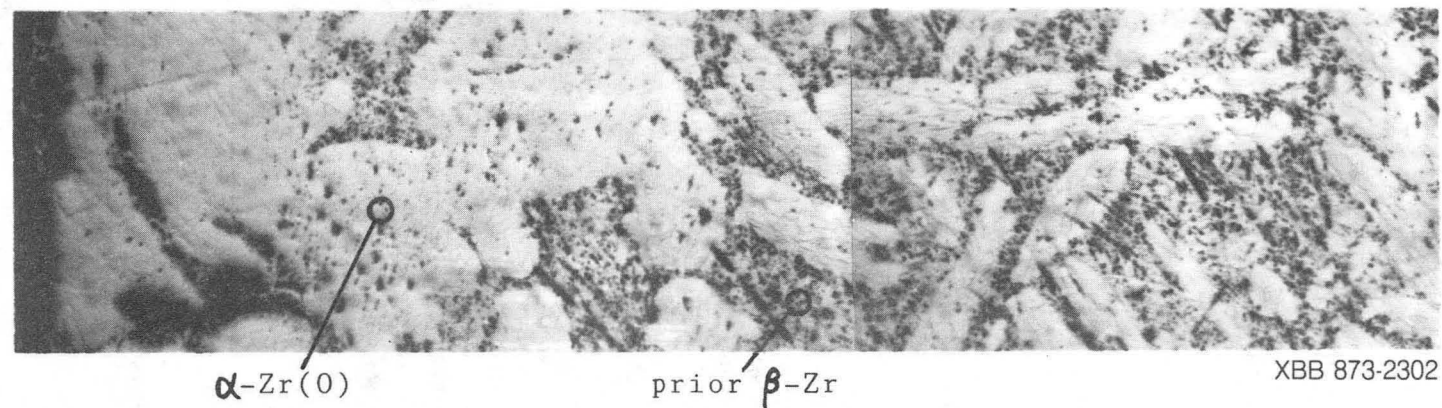


Fig. 2.1 Microstructure of 2.4 w/o O-Zry before and after homogenization.
(Homogenization condition ; $T=1500\text{ }^{\circ}\text{C}$, $t=3\text{ hrs}$)

2.1.3 ThO₂

In order to suppress natural convection in the UO₂/molten Zry reactions, a duplex crucible consisting of ThO₂ tube with UO₂ disk forming the bottom was designed. Y₂O₃ coating was applied to the inside of the ThO₂ tube to reduce possible reactions between the ThO₂ tube and the molten Zry. Thus, the crucible did not leak any molten metal during the experiments.

2.2 Apparatus

A schematic diagram of the experimental apparatus is shown in Fig. 2.2. The specimens are contained in a molybdenum crucible which is inductively heated. The molybdenum crucible consists of an upper cylindrical part with an upper lid but no bottom and a lower cylindrical part. The upper part is 16 mm in O.D., 1 mm thick, and 15 mm long. The lower part is 16 mm in O.D., 1 mm thick, and 7 mm long. The lid of the upper part has a hole 1 mm in diameter through which an optical pyrometer viewed the cavity formed by the assembly of the two parts. The lower part was designed to provide uniform temperature of the entire molybdenum crucible so as to meet the prerequisite condition for a good-quality black body hole.

Since the temperature range of the present experiment was above the melting point of alumina (~1900 °C), a zirconia insulator disk was inserted between the molybdenum crucible and the alumina block.

In order to keep the gaseous atmosphere slightly reducing, a premixed Ar - 5% H₂ mixture flushed the vessel during the experiment.

2.3 Temperature Measurement

The black hole temperature and the surface temperatures of the molybdenum susceptor were measured by an optical pyrometer using the top and the side windows shown in Fig. 2.2. The measured surface temperatures were corrected by using molybdenum emissivity(0.35) to obtain the true surface temperatures. Comparison of the black body hole temperature and

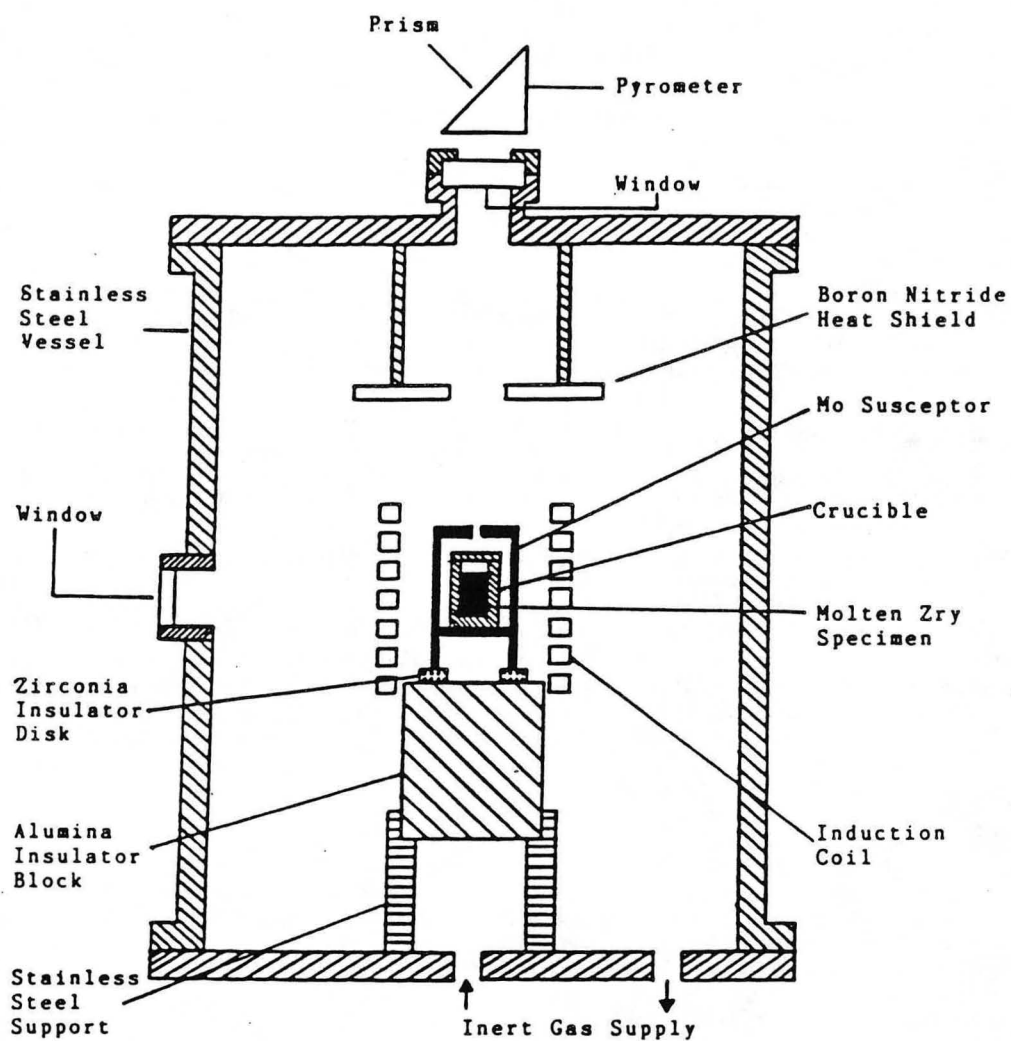


Fig. 2.2 Schematic Diagram of Experimental Apparatus.

the true surface temperature showed that the black body hole was of a good quality.

2.4 Heating and Cooling Curves

Heating and cooling curves are shown in Fig. 2.3. In this figure, position A represents the outer surface of the molybdenum crucible, position B the outer surface of the ThO_2 crucible, and position C the center of the Zry specimen. Temperature at position A was measured experimentally and corrected by using molybdenum emissivity to obtain the true temperature. Because of the thick-walled crucible design, the temperature of the molybdenum crucible was uniform to within 20 °C over its entire surface. Then, temperatures at positions B and C were calculated using the HEATING6 Code (22), based on the time-dependent temperatures of the molybdenum outer surface(position A). The latter was heated at 15 K/s from 1700 °C up to the temperature 100 °C higher than a desired reaction temperature. After being held here for a moment, it was cooled down to the desired temperature. This heating procedure gives a faster thermal response of the Zry specimen than that obtained by simply asymptotically approaching the final temperature.

2.5 Crucibles

Three types of Zry-containing crucible were tested (Fig. 2.4) :

- a) polycrystalline UO_2 crucible and lid
- b) ThO_2 side-wall and lid with a polycrystalline UO_2 disk forming the bottom
- c) ThO_2 crucible and lid containing a sphere UO_2 single crystal

In all designs, the lid was included to produce uniform heating of the Zry specimen.

The a-type crucible was designed to simulate more closely the vertical UO_2 surfaces with which the molten Zry is in contact during a melt-down event in reactor fuel. The results of a-type crucible experiments showed that there is a significant bulk motion of the

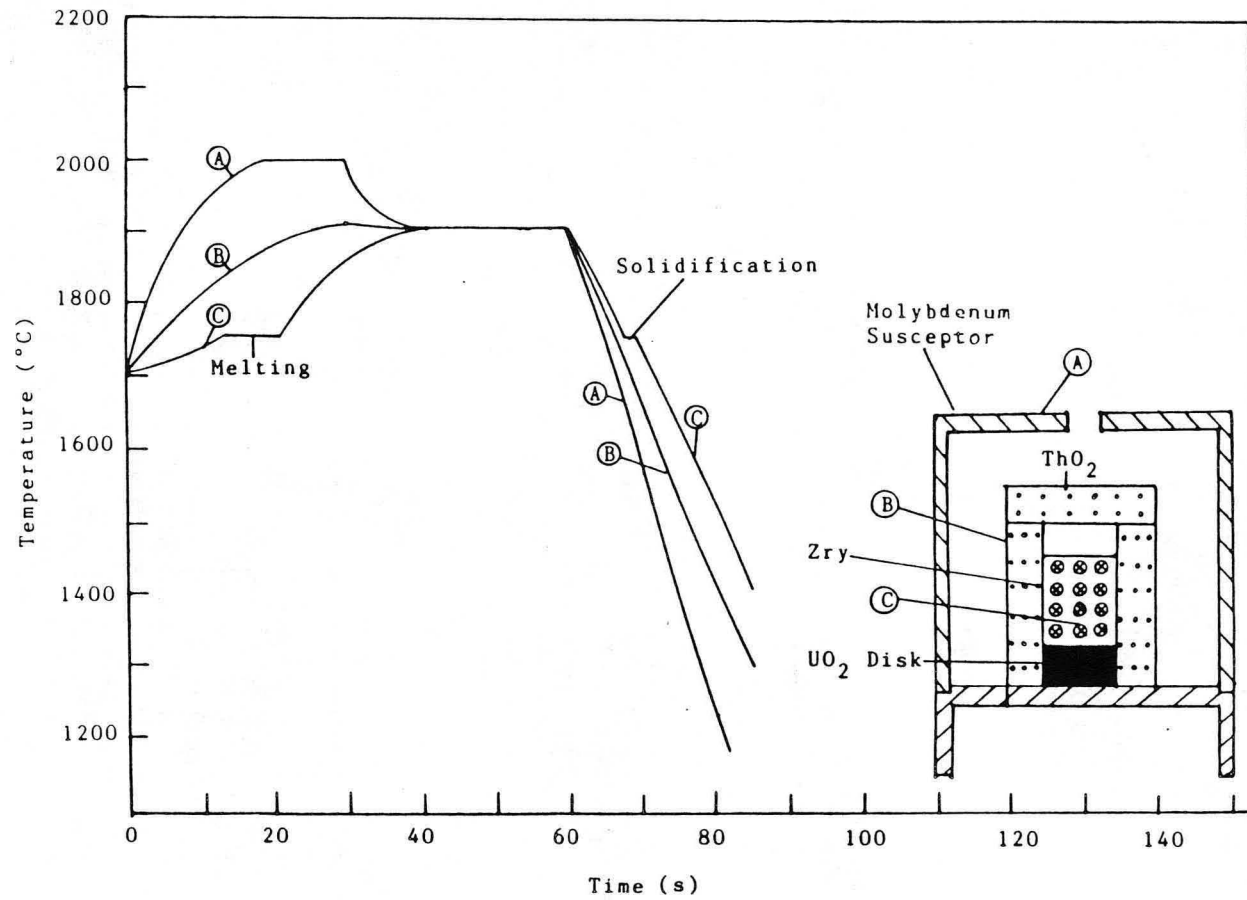


Fig. 2.3 Heating and Cooling Curves for duplex crucible. (The surface temperature at A was measured as a function of time and used in HEATING 6 to calculate the interior temperatures at B and C.)

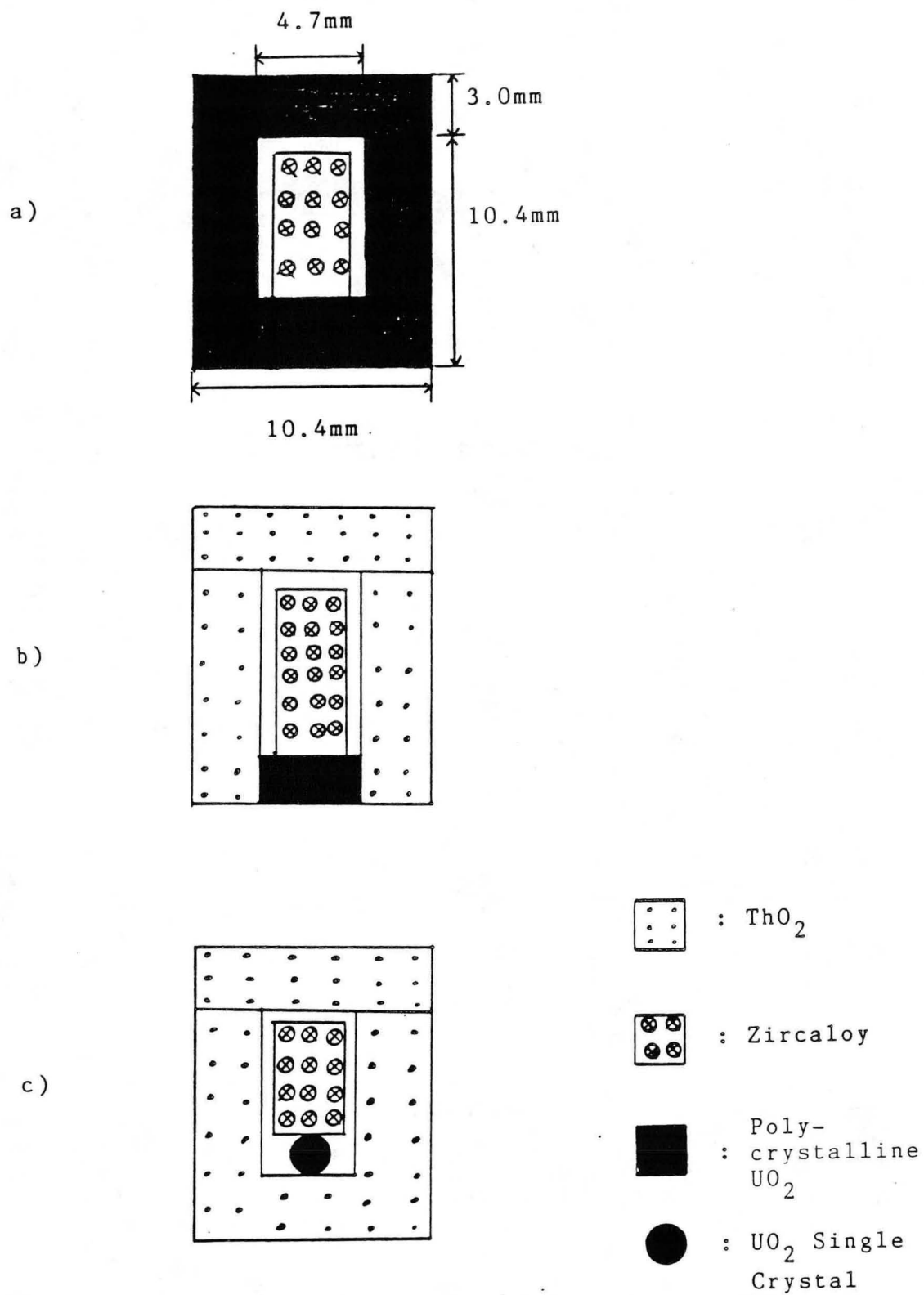


Fig. 2.4 Shapes and dimensions of three types of Zry-containing crucible.

molten metal caused by natural convection. The basis for this conclusion is the absence of a concentration gradient in the molten region, regardless of reaction temperature and time.

The b-type crucible was designed in order to investigate the one-dimensional diffusion process by suppressing natural convection which afflicts the a-type crucible. In b-type crucible, the uranium-containing reaction products, which has a higher density than the molten Zry, appear at the bottom. In addition, during cooling-down, the upper portion in the reaction zone is always hotter than the lower portion, which leads to decrease in liquid density on moving upwards. The results of the b-type crucible experiments confirmed that there is no strong natural convection, because definite reaction layers, each of which obeys the parabolic rate law, were observed.

The c-type crucible was designed to accommodate available single crystal spherical specimens, which were simply placed on the bottom of the ThO_2 crucible.

2.6 Analysis Tools

Several detection tools were used frequently in analyzing the samples : optical microscopy, scanning electron microscopy(SEM) with EDAX(energy dispersive analysis of X-rays), electron microprobe(EMP), X-ray fluorescence spectrometry(XFS), Auger electron spectroscopy(AES) and an image analyzer. In this section, the basic principles of each device are discussed.

2.6.1 Optical Microscopy

A Zeiss reflected-light microscope with differential interference contrast feature was used. The limitation of the optical microscope are : 1) The depth of focus is limited to about 1000 Å, so only a portion of polished surface appears in focus. 2) Only the phase contrast is shown, so the composition of each phase is not known.

2.6.2 Scanning Electron Microscopy(SEM) with EDAX

The basic principle behind the operation of the SEM is the use of a fine electron beam

striking the specimen. At the point of impact, a variety of phenomena occur, including production of secondary electrons, characteristic X-rays, Auger electrons, etc., which can be used to obtain information on the specimen surface. By scanning the electron beam in a raster pattern across the specimen surface in synchronization with a cathode X-ray tube, it is possible to map the specimen surface onto the display system. In EDAX, by using energy dispersive spectrometer, the identity and concentration of each element can be measured by the intensity of their characteristic X-rays. The EDAX analysis used standards for U, Th, Zr, Y and Sn. SEM has higher resolution, higher magnification(x30,000) and greater depth of focus than the optical microscopy. The combination of SEM and EDAX provides a tool to examine the topology and the elemental composition of the specimen surface. However, concentration of lighter elements(e.g., oxygen) cannot be determined by the EDAX analysis.

2.6.3 Electron Microprobe(EMP)

The electron microprobe is similar to SEM but the induced characteristic X-rays are analyzed by a wavelength spectrometer. The EMP analysis cannot detect oxygen but gives very accurate values for heavier elements(e.g. U). Oxygen content, therefore, can be determined by difference [$100 - (U + Th + Zr + Y + Sn)w/o$]. The EMP analysis used standards for U, ThO_2 , Zr, Y_2O_3 and Sn.

2.6.4 X-Ray Fluorescence Spectrometry(XFS)

The X-ray system is operated by the Instrument Technique Group at Lawrence Berkeley Laboratory. It consists of a low-power tungsten-anode X-ray tube, a silver secondary target to provide nearly monochromatic secondary excitation radiation, a silicon guard-ring reject detector and 1024 channel pulse height analyzer. The purpose of this instrument is to measure concentrations of certain elements over a large area(~ 1.2 cm in diameter). Concentrations of lighter elements(e.g., oxygen) cannot be determined by the XFS analysis. The XFS analysis used standards for U and Zr.

2.6.5 Auger Electron Spectroscopy(AES)

AES is similar to SEM but an electron of characteristic energy is analyzed instead of a characteristic X-ray. AES can be used to measure the average concentration of a certain region by scanning. The concentrations of lighter elements(e.g., oxygen) can be determined very accurately by AES analysis using suitable standards. The AES analysis used standards for U, Zr, UO_2 , and $\alpha\text{-Zr(O)}$ containing 5.0 w/o oxygen.

2.6.6 Image Analyzer

An image analyzer consists of a scanner, an analyzer module and a television monitor. The television monitor provides a high contrast image of the photomicrograph of the specimen being analyzed on a 9 inch-diagonal, high-resolution screen. An electrical signal which represents the image of the specimen to be analyzed is received by the analyzer module from the scanner. Analysis is initiated by the operator selecting the particles to be measured. An image analyzer provides a variety of quantitative measurements which include particle count, area, intercept count, area percentage, etc. These basic measurements permit determination of such useful materials parameters as : Number of particles per unit area, porosity, average ASTM grain size, and particle size distribution.

2.7 Specimen Preparation and Analysis Methodology

The sequence of specimen preparation and analyses is shown in Fig. 2.5. The reacted specimen was cut, ground, and polished with 1 and 6 μm diamond paste. In the as-polished specimen, metallic U and Zr are visible in the UO_2 region as shiny particles. In the air-oxidized specimen(several days exposure to air), the metallic U and the U in the (U,Zr) alloy oxidize to UO_2 (and appear black), while the metallic Zr particles remains shiny. Comparison of the as-polished specimen and the air-oxidized specimen thus shows the amount of Zr in the UO_2 region. Finally, an etching solution containing 40v/o nitric acid(1.42 sp.gr.) and 3v/o hydrofluoric acid(52%) was used to etch zirconium and to show definite boundaries between the reaction layers.

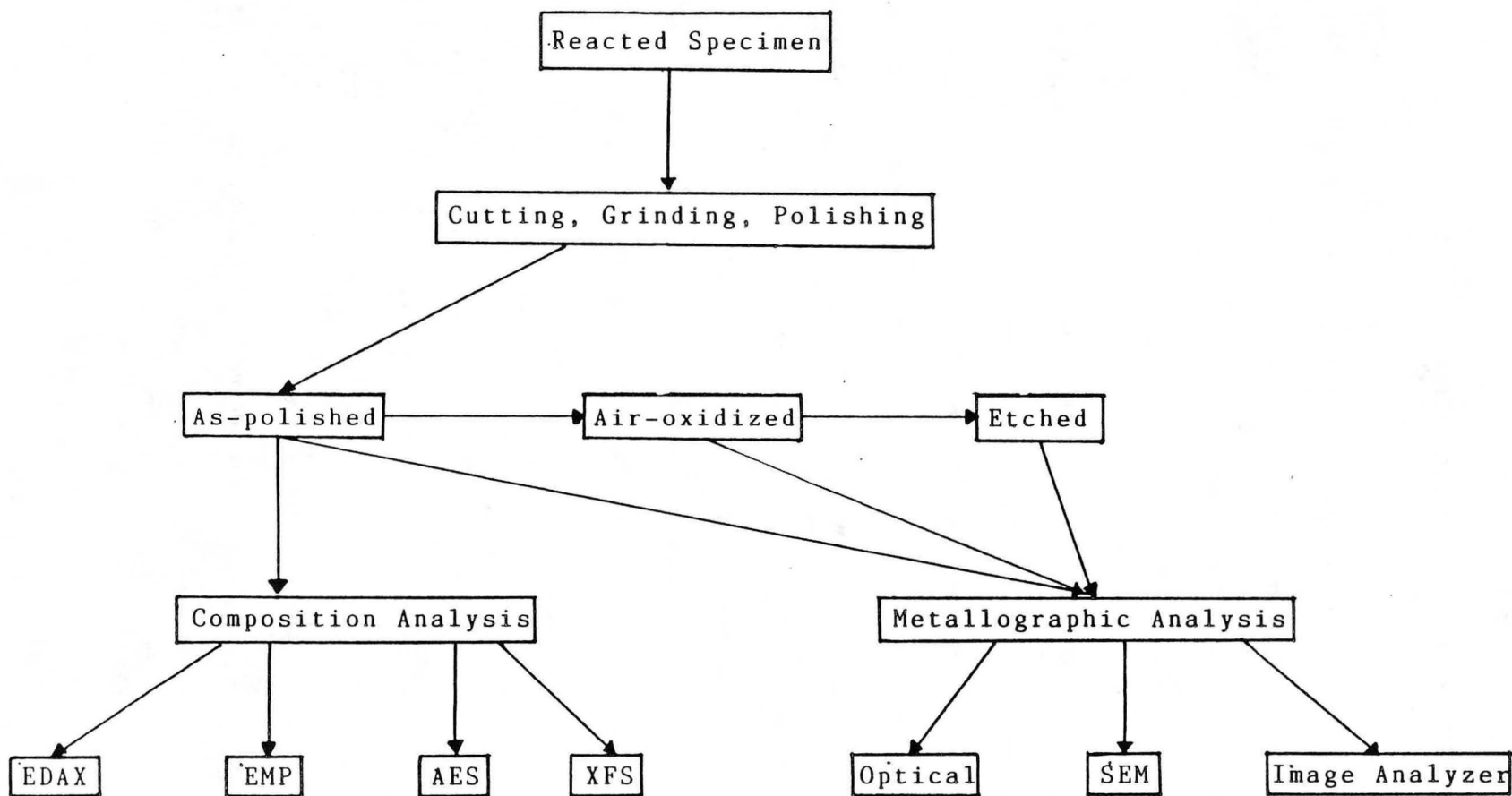


Fig. 2.5 Procedure of Specimen Analysis.

All specimens were examined metallographically to determine thicknesses of the various layers and their morphology. In addition, the porosity and the amount of the metallic precipitates in the UO_2 region were measured by using an image analyzer. Some specimens were examined by SEM with EDAX and EMP to identify the reaction products and to determine their compositions. AES was used to measure the overall average concentration over large areas perpendicular to the reaction interfaces. In addition, XFS was used to measure the concentration of uranium over a large area.

3. RESULTS

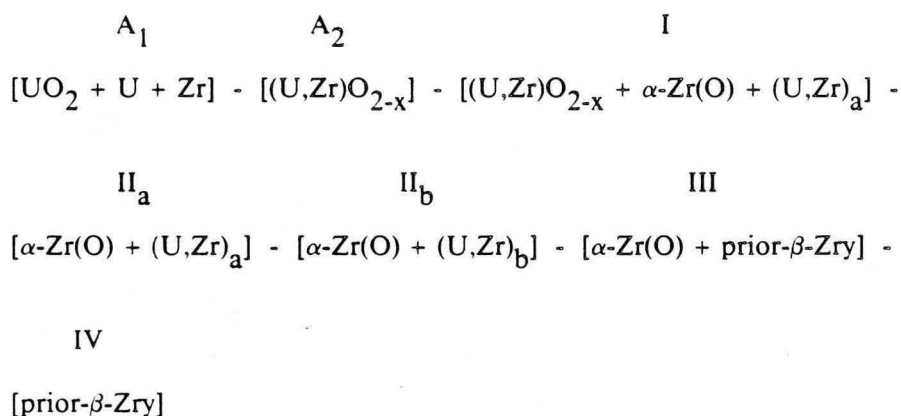
3.1 Polycrystalline UO_2 Disk/Molten Zry Reaction

3.1.1 Reaction Layers and Products

Optical photomicrographs and scanning electron micrographs were examined in the as-polished, the air-oxidized and the etched specimens. It was found that the number and the sequence of reaction layers are dependent on the initial oxygen content of the Zry. For the same initial oxygen content of the Zry, however, they are the same for all temperatures and times tested. In this section, the optical and SEM observations of the polished specimens are presented and discussed.

A) UO_2 /Pure Zry Reaction

Fig. 3.1 shows the near-interface regions following interaction of UO_2 with pure Zry. The anneal was conducted for 20 s at 2000 °C. The room temperature sequence of the individual reaction layers for the initially oxygen-free Zry is :



At the reaction temperature, regions A_1 and A_2 were a solid phase, region I was a mixture of a solid phase and a liquid phase, and regions II_a through IV were a single liquid.

It is important to note that the layer sequences following cool-down are not those which existed at the reaction temperatures. The reaction temperature sequence of the individual

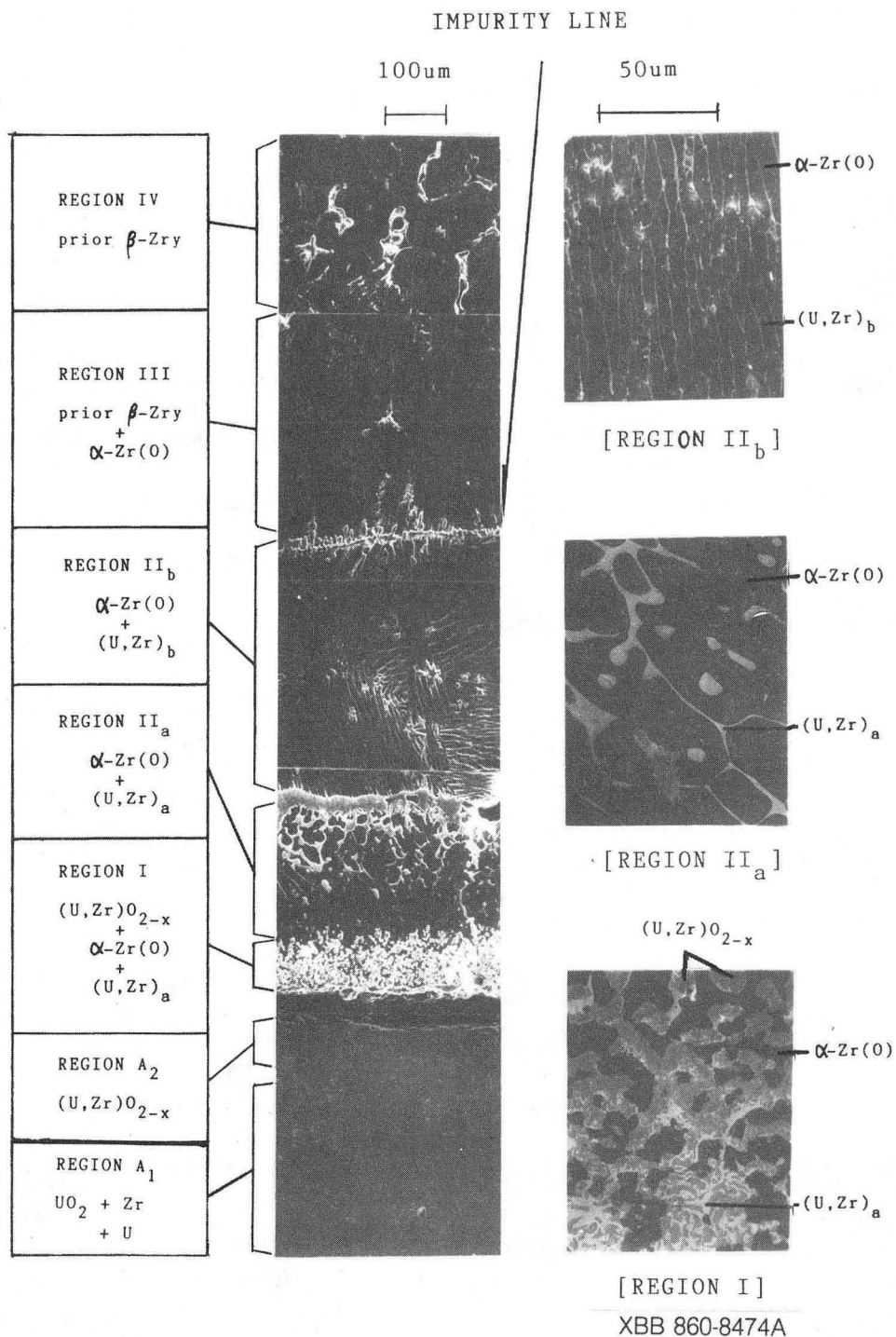


Fig. 3.1 UO_2 /Pure Zry Reaction Layer(SEM).
($T=2000^\circ\text{C}$, $t=20\text{s}$)

reaction layers will be discussed in section 4.1.

The UO_2 region is divided into two distinct regions, A_1 and A_2 . The boundary between A_1 and A_2 , however, is not a true interface ; rather it separates portions of U-Zr ternary oxide with different amounts of substitutional Zr and metal precipitation. As shown in Fig. 3.2, region A_1 in the as-polished specimen has a higher porosity and a higher density of shiny particles than region A_2 . In addition, porosity and shiny particles in region A_1 are uniformly distributed and most of shiny particles are associated with pores. On the other hand, region A_1 in the air-oxidized specimen(see Fig. 3.2) shows that a few of the shiny particles in the as-polished specimen are $\alpha\text{-Zr(O)}$ but the majority are uranium. The zirconium particles are always associated with pores. The detailed view of region A_2 shown in Fig. 3.3 reveals the pores in region A_2 filled with $\alpha\text{-Zr(O)}$.

The microstructural appearance of region I [$(\text{U,Zr})\text{O}_{2-x} + \alpha\text{-Zr(O)} + (\text{U,Zr})$] was strongly dependent on the initial oxygen content of the Zry. The schematic diagram of the microstructural appearance of region I is shown in Fig. 3.4. This figure shows a porous-medium-like structure, a channel structure and separate particles of $(\text{U,Zr})\text{O}_{2-x}$. The characteristic layer structure of region I is shown in Fig. 3.5. In this figure, $\alpha\text{-Zr(O)}$ appears dark gray, $(\text{U,Zr})\text{O}_{2-x}$ ⁶ medium gray and (U,Zr) light gray. This figure shows that the porous-medium-like structure is apparent near the A_2/I interface. On moving upwards in region I, the porous-medium-like structure changes to the channel structure and finally to the separate particles of $(\text{U,Zr})\text{O}_{2-x}$. (U,Zr) and/or $\alpha\text{-Zr(O)}$ channels are visible at the A_2/I interface as well as through region I. From the microstructure of region I, it was found that on moving upwards in region I(i.e. to the left in Fig. 3.5) the particle size and volume fraction of $(\text{U,Zr})\text{O}_{2-x}$ decrease. Region I is shown in Fig. 3.6 as a function of reaction temperature. This figure shows that the channel structure become much more apparent as reaction temperature increases.

[6] Approximate value of the O/M ratio in $(\text{U,Zr})\text{O}_{2-x}$ is 1.8(see Table 2).

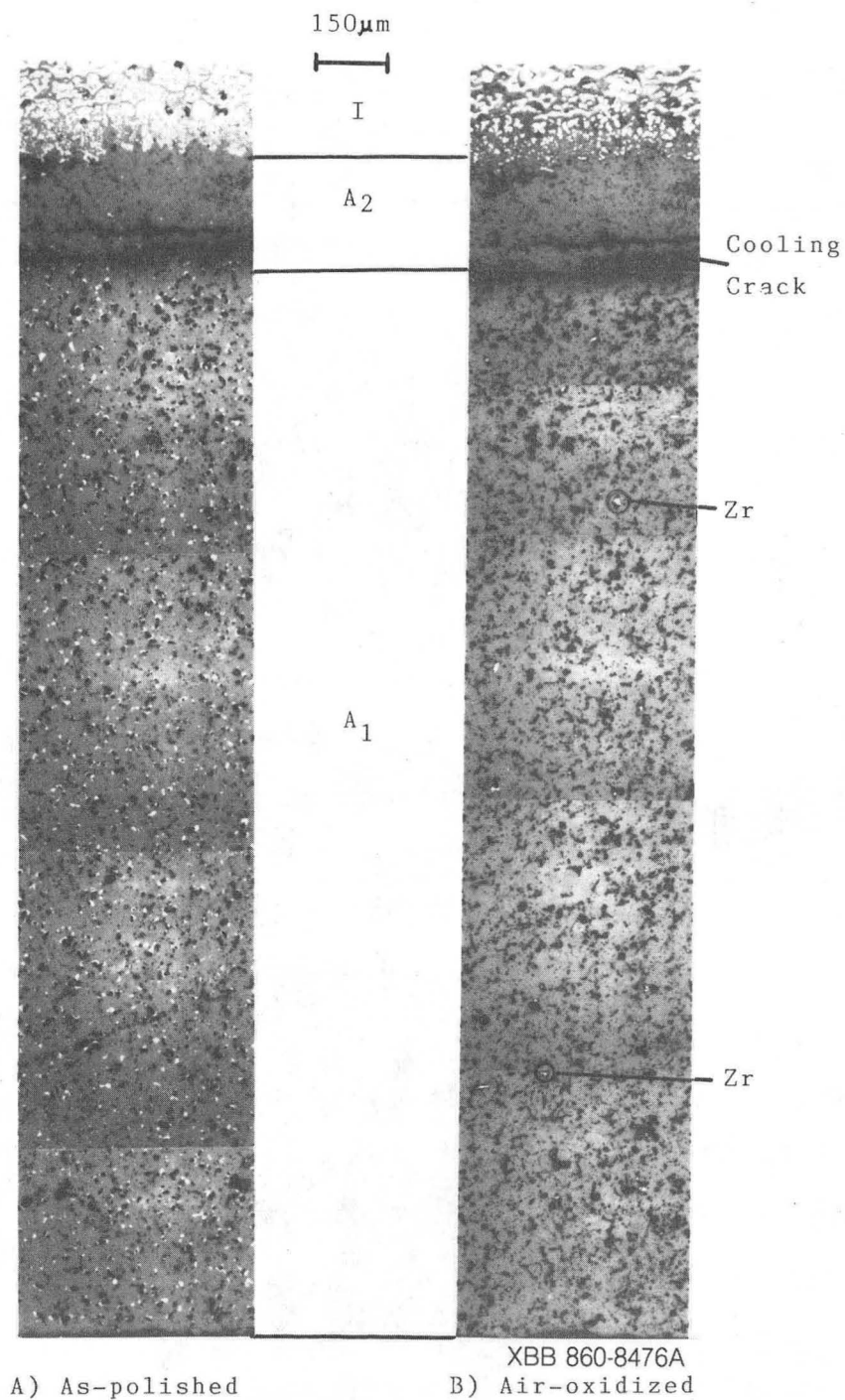


Fig. 3.2 Microstructural Differences between A₁ and A₂ for the UO₂/Pure Zry System (Optical). (T=2100°C, t=120s)

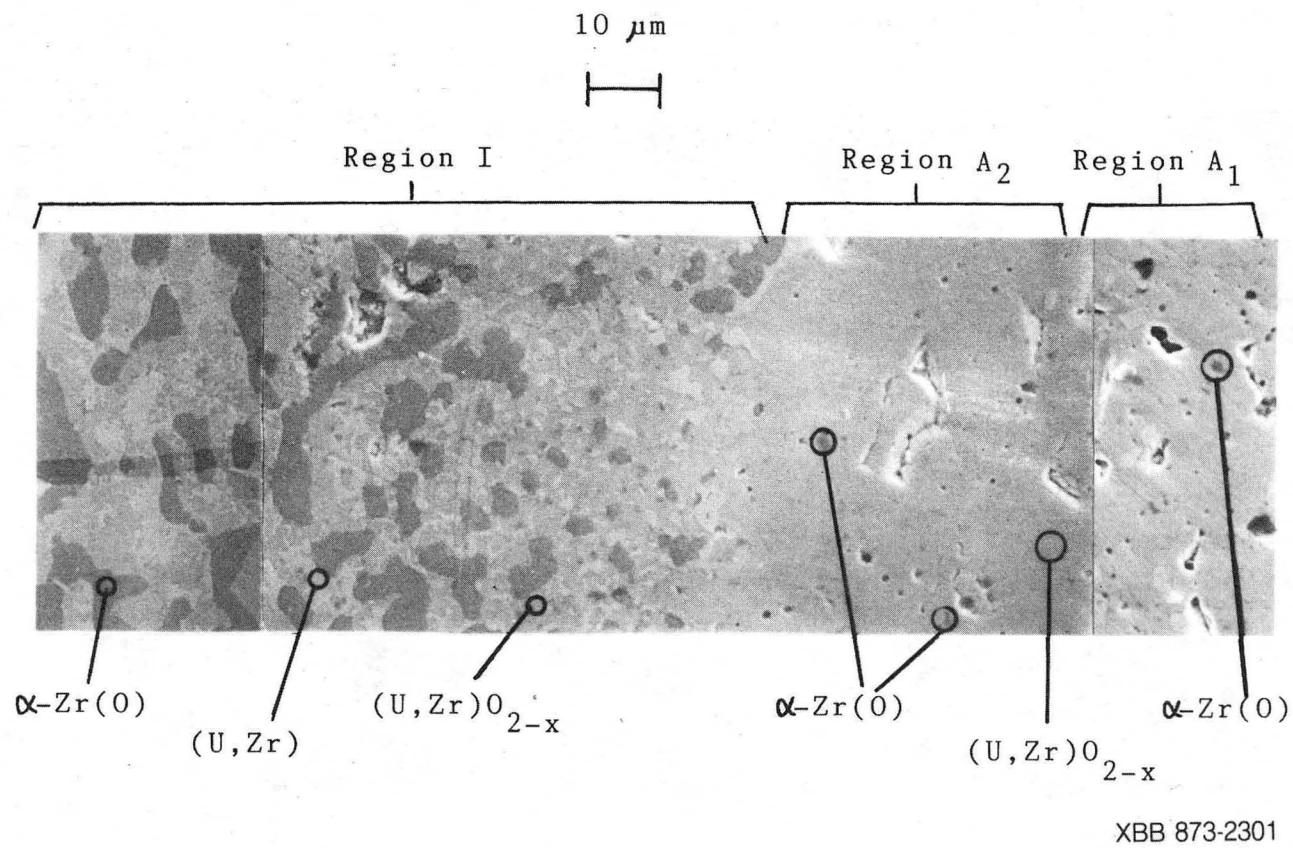


Fig. 3.3 UO_2 /Molten Zry Interface Appearance(SEM). ($T=2100^\circ\text{C}$, $t=120\text{ s}$)

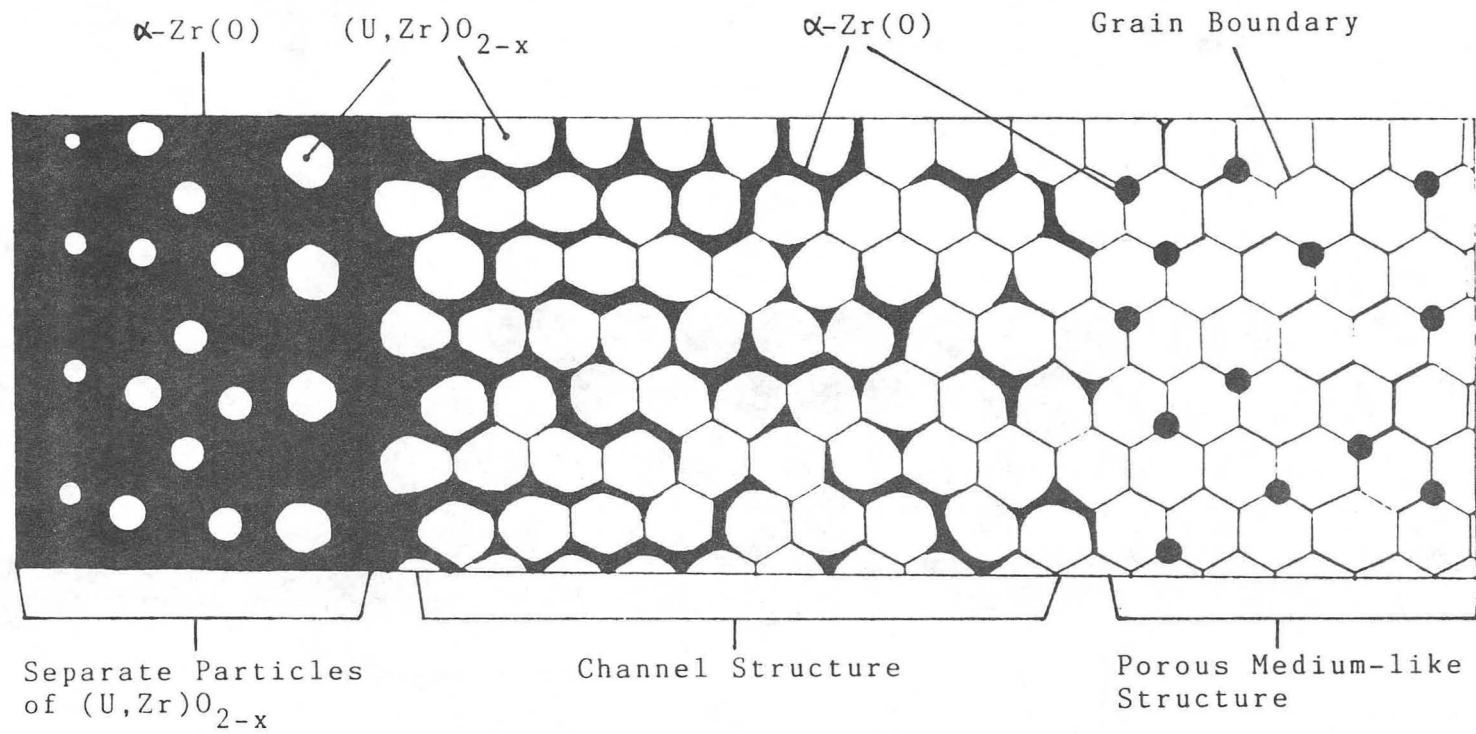


Fig. 3.4 Schematic Diagram of the Microstructural Appearance of Region I for the UO_2 Disk/Molten Zry System.

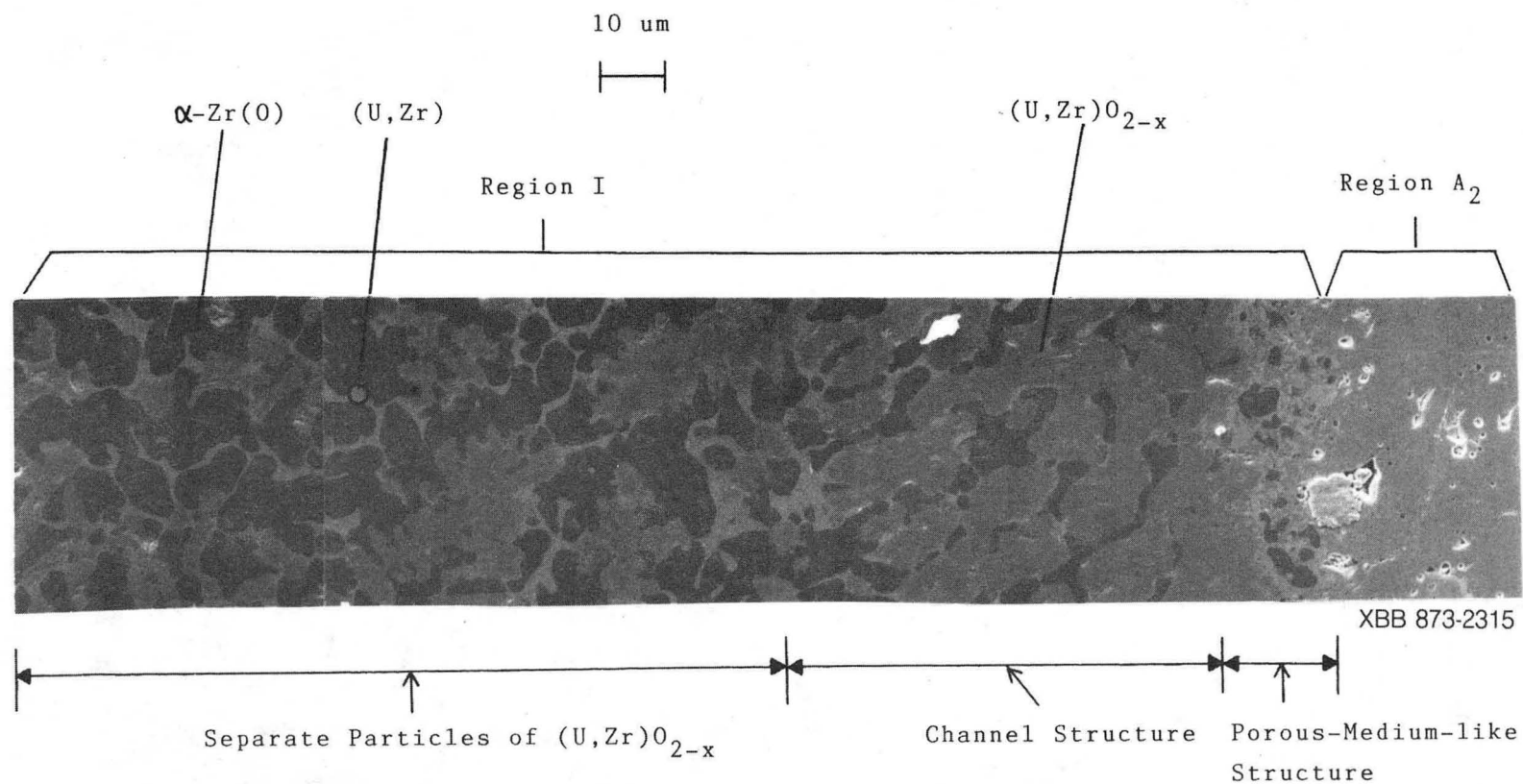


Fig. 3.5 Microstructure of Region I for the UO_2 Disk/Pure Zry System(SEM).
 ($T=2200^\circ\text{C}$, $t=120\text{ s}$)

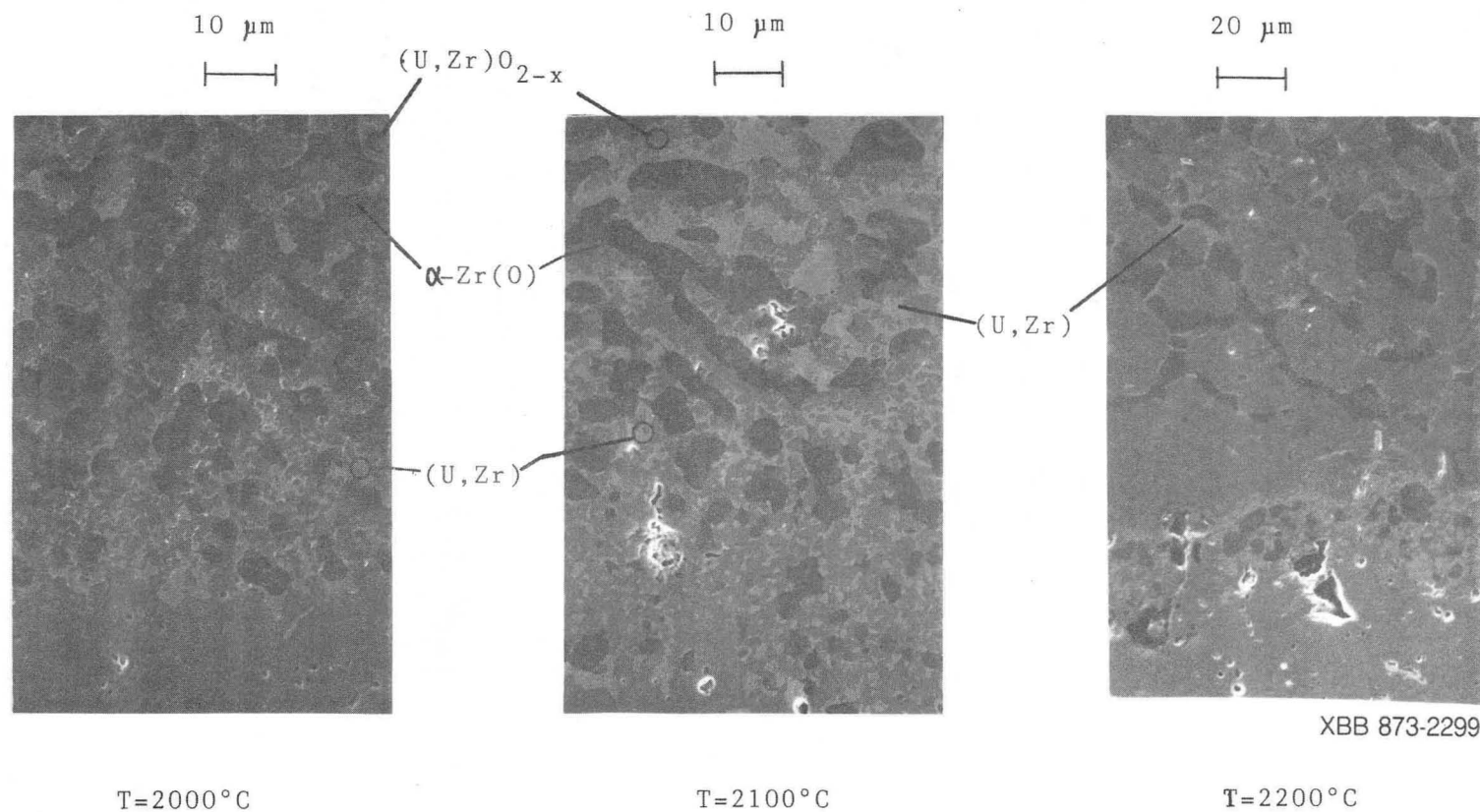


Fig. 3.6 Microstructural Appearance of Region I for UO_2 /Pure Zry System as a Function of Reaction Temperature(SEM). (t=120 s)

Fig. 3.7 shows the nature of regions II_a and II_b . These regions are composed of α -Zr(O)(dark gray) and (U,Zr)(light gray) in the SEM micrograph with quite different compositions and are separated by an abrupt microstructural change.

The U content in the (U,Zr) alloy in region II_a is above 80 w/o while in region II_b it is below 65 w/o (see Table 2). The compositional difference shows that region II_a represents $[\alpha\text{-Zr(O)} + \text{L}]$ and region II_b $[\text{Zr(O)} + (\gamma\text{-U}, \beta\text{-Zr})]$ in the U-Zr-O isothermal section at 1500 °C (see Fig. 1.1) (presumably, these two-phase zones formed during cooling and were frozen at about 1500 °C). However, the composition of the (U,Zr) alloy around the II_a/II_b interface is between 65 and 80 w/o U. On moving from the region II_a to II_b , therefore, there is a continuous compositional change even though there is an abrupt microstructural change.

Region II_a has an equiaxed microstructure of α -Zr(O) grains surrounded by (U,Zr) rich in U (see point A in Fig. 3.7). The equiaxed microstructure requires a considerable amount of nucleation which occurs with relatively rapid supercooling. These nuclei (α -Zr(O)) have higher melting points than any subsequently-formed solid, so that the successive layers of the solid phase deposited on these nuclei are a little richer than its predecessor in the low-melting component, U. The final solid is composed of a cored structure in which each equiaxed particle has a high-melting central portion (α -Zr(O)) surrounded by lower melting (U,Zr).

Region II_b consists of very fine (U,Zr) flat platelets in an α -Zr(O) matrix. This microstructure usually forms in eutectic alloys under conditions in which the interfacial energies of two phases are low and the cooling rate is small enough to maintain planar growth fronts (23). With these prerequisite conditions, it is also possible to solidify alloys with plane fronts such as lamellar, rod and flat platelets that undergo a peritectic reaction or a monotectic reaction on solidification (24,25). Comparison of Zr-ZrO₂ phase diagram with the (U,Zr,O) isothermal section from 1500 to 1950 °C (see Fig. 1.1) shows that $[\alpha\text{-Zr(O)} + (\gamma\text{-U}, \beta\text{-Zr})]$ is formed by a peritectic reaction. In addition, the interfacial energy between α -Zr(O) and $(\gamma\text{-U}, \beta\text{-Zr})$ is quite low (26). Region II_b , therefore, shows the flat platelet microstructure. The II_b/III interface is not apparent even though region III contains no (U,Zr) alloy

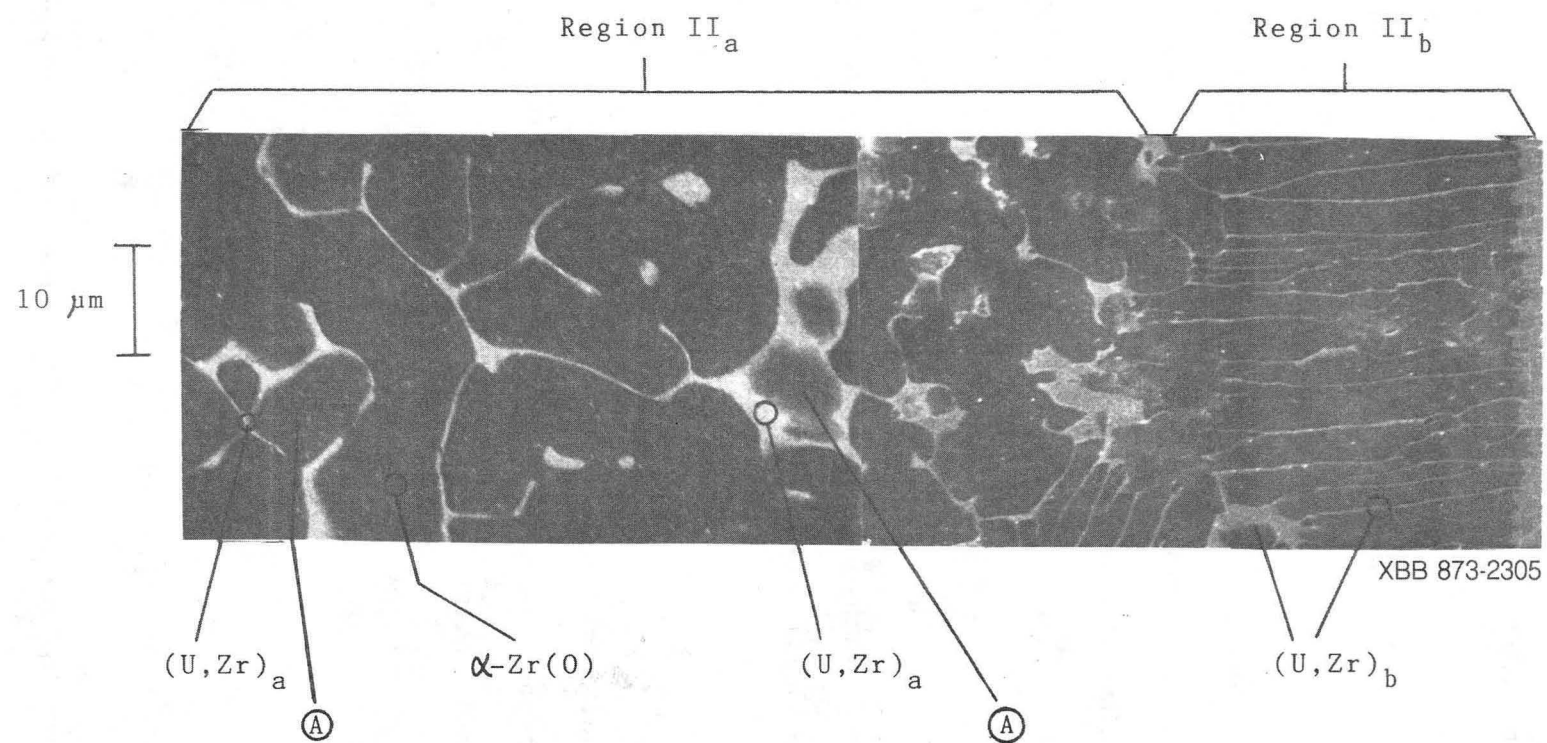


Fig. 3.7 Microstructural Differences between Region II_a and II_b(SEM).
(T=2000°C, t=25 s)

along the grain boundaries.

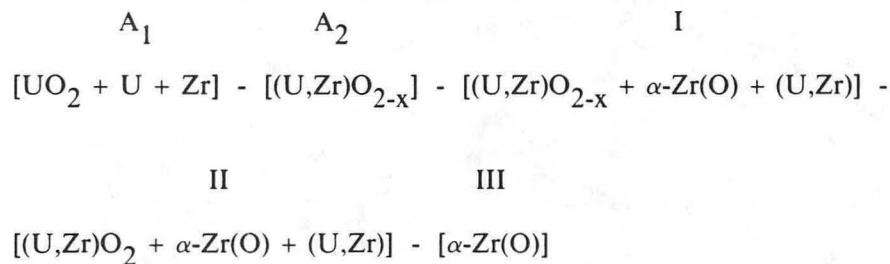
Region III consists of α -Zr(O) and prior β -Zry. These two phases are distinguishable in the Zr-etched specimens, because prior β -Zry shows a Widmannstatten structure.

Region IV consists of prior β -Zry. However, it is very difficult to identify the III/IV interface, because the interface is very irregular in places where prior β -Zry incursions extends into α -Zr(O).

There is a definite line of impurities which consists mostly of Y_2O_3 and ThO_2 (see Fig. 3.1). The impurities originate from the Y_2O_3 coating on the ThO_2 crucible. The distance from the A_2/I interface to the impurity line is around 500 μm . This distance is independent of reaction time but depends slightly on reaction temperature. The distinct line is formed by a "pushing" mechanism caused by solid-liquid interface growth during cooling. Uhlmann et al(27) have shown that impurities in liquid can be pushed by the liquid-solid interface only if the growth velocity is below the critical velocity and a certain interfacial energy relationship between liquid phase and solid impurity is satisfied.

B) $UO_2/2.4w/o$ O-Zry Reaction

Fig. 3.8 shows the near-interface regions following interaction of UO_2 with Zry containing 2.4w/o oxygen. The anneal was conducted for 120 s at 2000 °C. The room temperature sequence of the individual reaction layers for the 2.4w/o O-Zry is :



At the reaction temperature, regions A_1 and A_2 were a solid phase, region I was a mixture of a solid phase and a liquid phase, and regions II and III were a single liquid.

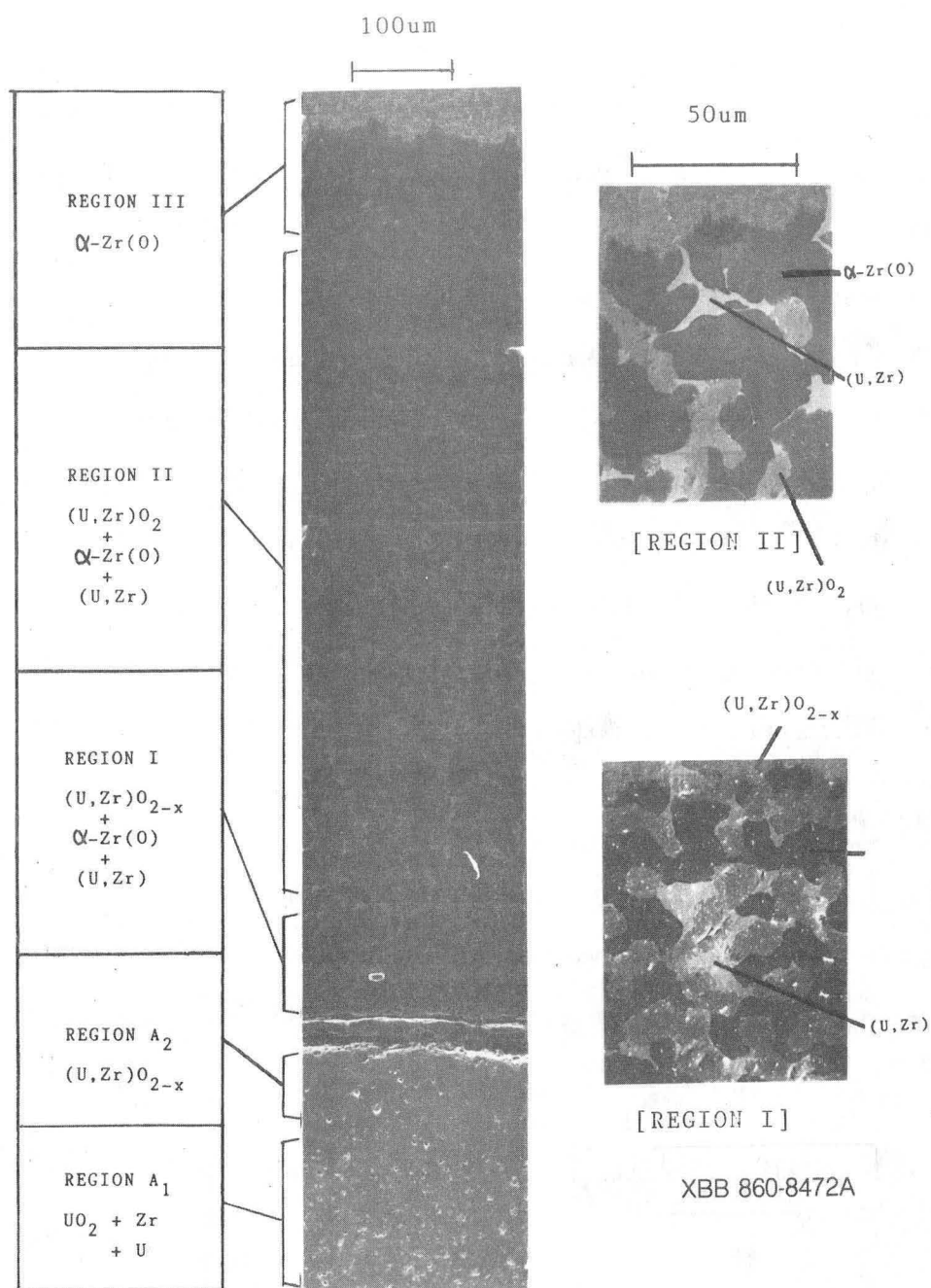
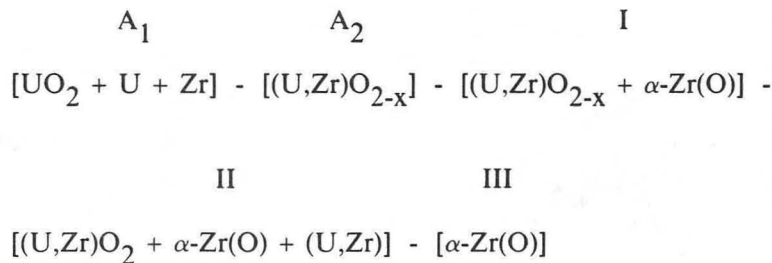


Fig. 3.8 $\text{UO}_2/2.4\text{w/o O-Zry}$ Reaction Layer(SEM).
($T=2000^\circ\text{C}$, $t=120\text{s}$)

The appearances of regions A_1 , A_2 and I are exactly the same as those for the reaction with pure Zry. Region I is shown in Fig. 3.9 as a function of reaction temperature. As explained in section 3.1.1 A, this figure shows that the porous-medium-like structure and the channel structure become much more apparent as reaction temperature increases. Region II (see Fig. 3.8) is composed of α -Zr(O), (U,Zr) and (U,Zr)O₂. The (U,Zr)O₂ phase is distinguishable from the (U,Zr)O_{2-x} phase in region I microstructurally and chemically. The (U,Zr)O_{2-x} phase exhibited the characteristic microstructure (Fig. 3.5), while the (U,Zr)O₂ phase formed thin bands in the α -Zr(O) matrix (Fig. 3.8), which indicates that the (U,Zr)O₂ particles in region II were precipitated from the (U,Zr,O) melt during cooling-down. In addition, the EMP analysis showed the (U,Zr)O_{2-x} to be hypostoichiometric (O/M=1.8) and the (U,Zr)O₂ stoichiometric (O/M=2). Fig. 3.8 shows that the fraction of the (U,Zr)O₂ decreases on moving upwards in region II. The II/III interface is not distinct even though there is no (U,Zr) or (U,Zr)O₂ in region III.

C) UO₂/5.0w/o O-Zry Reaction

Fig. 3.10 shows the near-interface regions following interaction of UO₂ with Zry containing 5.0w/o oxygen. The anneal was conducted for 80 s at 2000 °C. The room temperature sequence of the individual reaction layers for the 5.0w/o O-Zry is :



At the reaction temperature, regions A_1 and A_2 were solid phase, region I was a mixture of a solid phase and a liquid phase, and regions II and III were a single liquid.

The appearances of region A_1 and A_2 are exactly the same as those for the 2.4w/o O-Zry as well as the pure Zry. Region I, however, is composed only of (U,Zr)O_{2-x} and α -Zr(O) ;

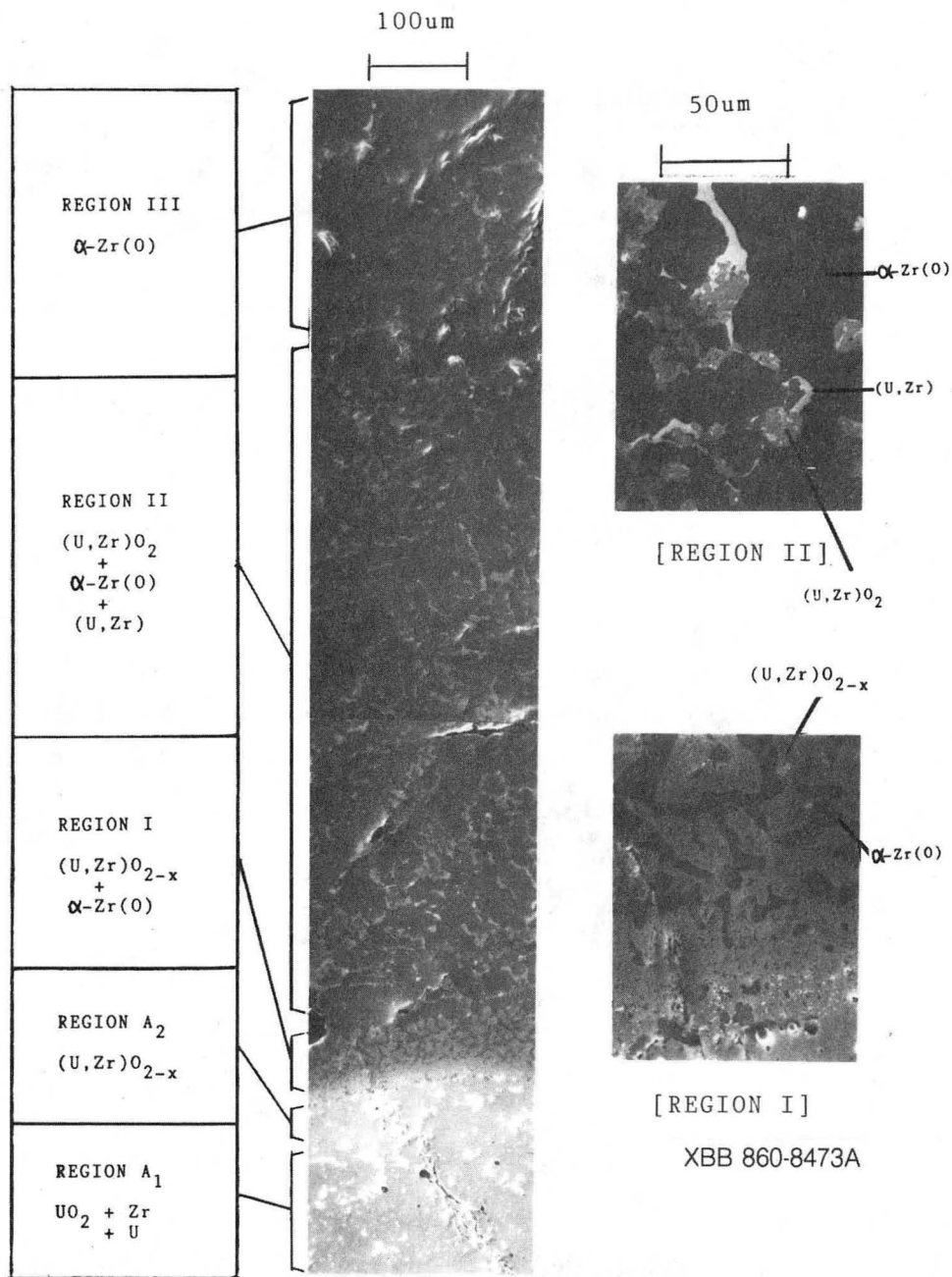


Fig. 3.10 $\text{UO}_2/5.0\text{w/o O-Zry}$ Reaction Layer(SEM).
($T=2000^\circ\text{C}$, $t=80\text{s}$)

the (U,Zr) phase is absent. Region I is shown in Fig. 3.11 as a function of reaction temperature. This figure shows that the porous-medium-like structure is mixed with the channel structure, in contrast to Figs. 3.6 and 3.9.

Fig. 3.12 shows the nature of region II for the pure Zry, the 2.4w/o O-Zry and the 5.0w/o o-Zry, respectively. This figure indicates that the $(U,Zr)O_2$ increases and the (U,Zr) decreases as the initial oxygen content of the Zry increases.

3.1.2 Elemental Concentration Distribution

The U, Zr, O concentrations in the individual reaction products were determined by energy dispersive X-ray analysis(EDAX) and electron microprobe(EMP). The oxygen content of the reaction products was determined by difference $[100 - (Zr + U + Y + Th + Sn)w/o]$ from the EMP analysis. The oxygen concentrations measured by AES agreed well with those determined by EMP. The EMP analysis shows that thorium content of the α -Zr(O) reaction product is less than 0.1 w/o ; yttrium is not detectable. Therefore, the effect of ThO_2 crucible and Y_2O_3 coating on the compositions of the reaction products is negligible. The tin content of the α -Zr(O) is about 1.5w/o. The EMP and EDAX results for the individual phases in the polycrystalline UO_2 disk/molten Zry system are shown in Tables 2 through 4. The ranges in the entries in these tables represent composition variations over the thicknesses of the various layers.

Tables 2 through 4 shows that a zirconium concentration gradient in the $(U,Zr)O_{2-x}$ phase exists across region I. The $(U,Zr)O_{2-x}$ contains up to 10 w/o Zr and 13 w/o oxygen. The oxygen concentration in the α -Zr(O) matrix from region I to region II is relatively uniform, compared with the U and the Zr concentrations, as shown in Tables 2 through 4. These tables show that the α -Zr(O) in regions I and II contains up to 6 w/o oxygen and 6 w/o U. From Table 2, the prior β -Zry in region IV contains up to about 2.5 w/o oxygen and very small amount of U.

Tables 2 through 4 show that, in general, the (U,Zr) contains no oxygen. Table 2

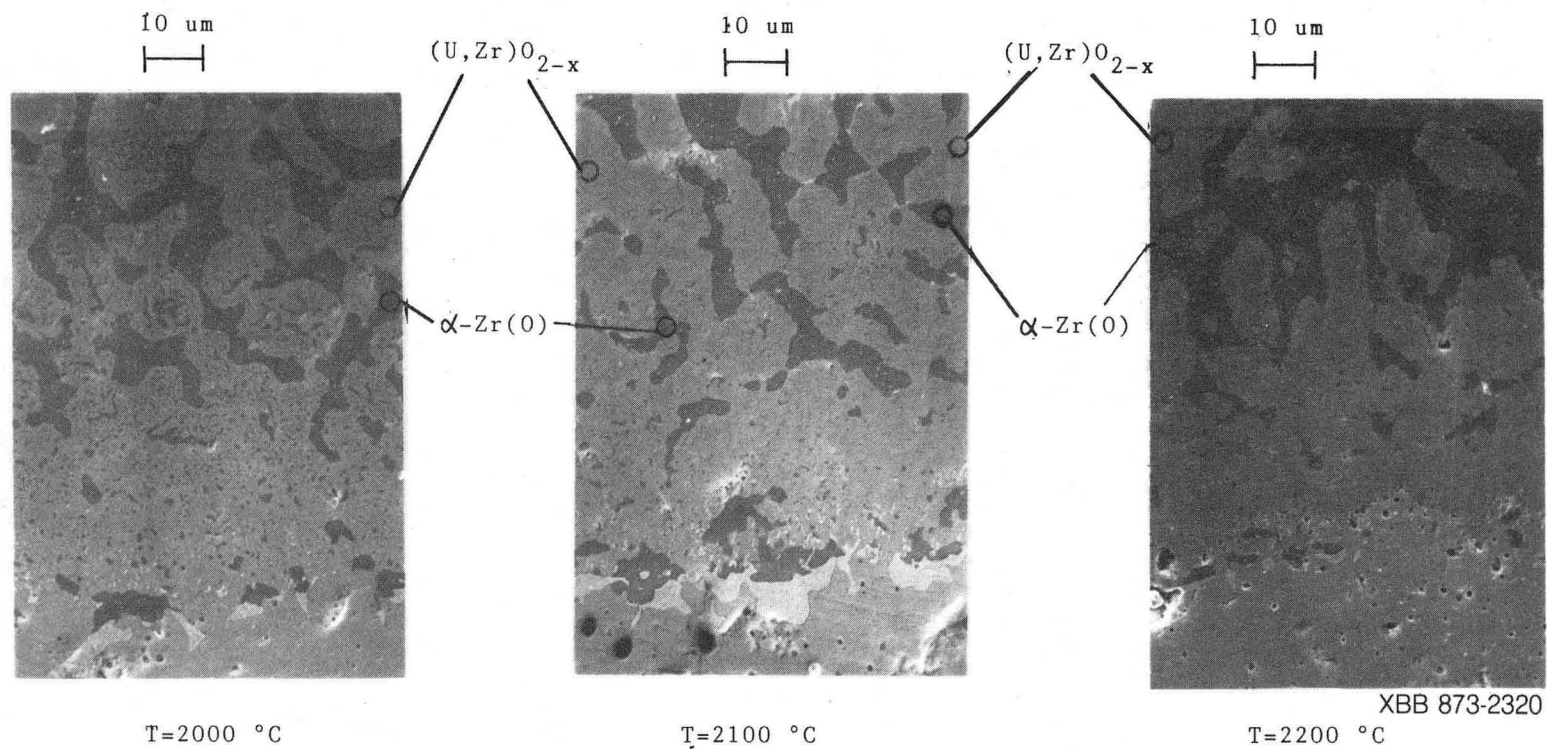


Fig. 3.11 Microstructural Appearance of Region I for $UO_2/5.0w/o$ O-Zry System as a Function of Reaction Temperature(SEM). ($t=120$ s)

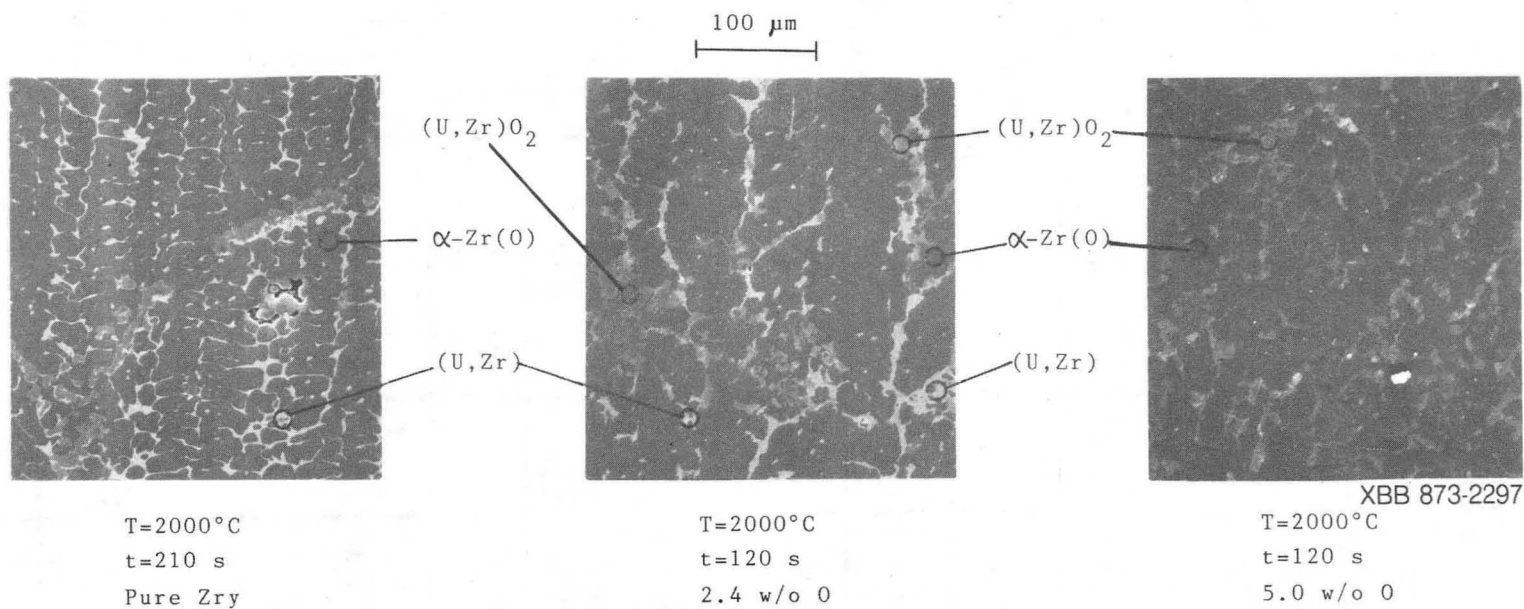


Fig. 3.12 Microstructure of Region II(SEM).

Table 2 Compositions for the polycrystalline UO_2 disk/pure Zry system determined by EMP and EDAX analysis(in wt %)*.

			Region A ₂	Region I				Region II _a		Region II _b		Region III	Region IV	
Temp. (°C)	Time (s)	Element	(U,Zr)O _{2-x}	(U,Zr)O _{2-x}	(U,Zr)		α-Zr(O) [#]	(U,Zr)	α-Zr(O) [#]	(U,Zr)		α-Zr(O) [#]	α-Zr(O) [#]	prior β-Zry
			EMP	EMP	EMP	EDAX	EMP	EDAX	EMP	EMP	EDAX	EMP	EMP	EMP
2000	10	U		79-83			5	88-92	4	65	62	2	1	1
		Zr		5-9			91	8-12	92	35	38	94	96	99
		O		12			4		4			4	3	1
	25	U		75-82		97-99	5	86-90	5		63	1	1	1
		Zr		6-12		1-3	90	10-14	91		36	95	95-96	98
		O		12-13			5		4			4	3-4	1
2100	10	U	90				5	85-90	4		60-66	2	1	1
		Zr	**				89	10-15	90		34-40	94	95-96	98
		O	10				6		6			4	4	1
	30	U	89	80-83	96-99	96-98	5	78-90	5		54-63	1	1	1
		Zr	**	5-8	1-4	2-4	90	10-22	91		37-46	96	95-96	98
		O	11	12			5		4			3	3-4	1

* : Oxygen by difference [100 w/o - (U + Zr + Th + Y + Sn)w/o]

** : Less than the detection limit of EMP

: Also contains 1.5w/o Sn

Table 3 Compositions for polycrystalline UO_2 disk/2.4w/o O-Zry system from EMP analysis (in wt %)*

Temp. (°C)	Time (sec)	Element	Region A ₂	Region I		
			(U,Zr)O _{2-x}	(U,Zr)O _{2-x}	(U,Zr)	α-Zr(O)
2000	120	U	89	82 - 84	97	5
		Zr	**	4 - 5	3	89
		O	11	12		6
			Region II			Region III
			(U,Zr)O ₂	(U,Zr)	α-Zr(O)	α-Zr(O)
		U	13	89	6	
		Zr	63	11	88	95 - 97
		O	24		6	3 - 5

* Oxygen by difference [100 - (U + Zr + Sn)w/o]

** Less than the detection limit of EMP

Table 4 Compositions for polycrystalline UO_2 disk/5.0w/o O-Zry system from EMP analysis (in wt %)*

Temp. (°C)	Time (sec)	Element	Region A ₂	Region I	
			(U,Zr)O _{2-x}	(U,Zr)O _{2-x}	α-Zr(O)
2000	120	U	89	80 - 82	5
		Zr	**	5 - 7	89
		O	11	13	6
			Region II		Region III
			(U,Zr)O ₂	(U,Zr)	α-Zr(O)
		U	13	90	5
		Zr	63	10	89
		O	24		6
					94 - 95
					5 - 6

* Oxygen by difference [100 - (U + Zr + Sn)w/o]

** Less than the detection limit of EMP

shows that the Zr content in the (U,Zr) increases across region II_a, becoming as large as 22w/o Zr. In moving from II_a to II_b region, there is a continuous compositional change in the (U,Zr) phase. The (U,Zr) phase in region II_b contains a nearly constant concentration of 34 w/o Zr. Tables 2 and 3 show that the (U,Zr) near the A₂/I interface contains up to about 4 w/o Zr.

Comparison of Table 2 through 4 shows that there are no significant differences between the element distributions in the various layers except in region II. The (U,Zr)O₂ phase appears in region II for the 2.4 w/o O-Zry and the 5.0 w/o O-Zry systems in contrast to that for the pure Zry system, in which the ternary oxide is absent in region II. The (U,Zr)O₂ in region II contains about 63 w/o Zr and 24 w/o oxygen. Region III for the 5.0 w/o O-Zry system contains more oxygen than the same region for the 2.4 w/o O-Zry system, which in turn is richer in oxygen than region III for the pure Zry system.

AES was used to measure the overall average concentration perpendicular to the reaction interface. The average concentration of a certain region was obtained by scanning over that region. The results of the AES analysis are shown in Figs. 3.13 through 3.15 for the various initial oxygen contents of the Zry. These overall average concentration distributions produce the diffusion paths on the ternary isothermal section at 2000 °C, as shown in Fig. 3.16, even though the results shown in Figs. 13-15 are for 2100 °C. Unfortunately, the ternary isothermal section at 2100 °C has not been reported. Comparison of the quasi-binary section between UO₂ and α-Zr(O) at 2000 and 2100 °C (see Fig. 1.2) indicates that there are no significant differences in the existing phases and the relative ratio of these phases. The ternary isothermal section at 2000 °C, therefore, was used to plot the data at 2100 °C.

3.1.3 Kinetics of Layer Growth

The extent of the layer growth depends on reaction temperature, reaction time and the initial oxygen content of the Zry. The visual appearance of the layers for the UO₂/pure Zry reaction is shown in Fig. 3.17 for various times at 2000 °C.

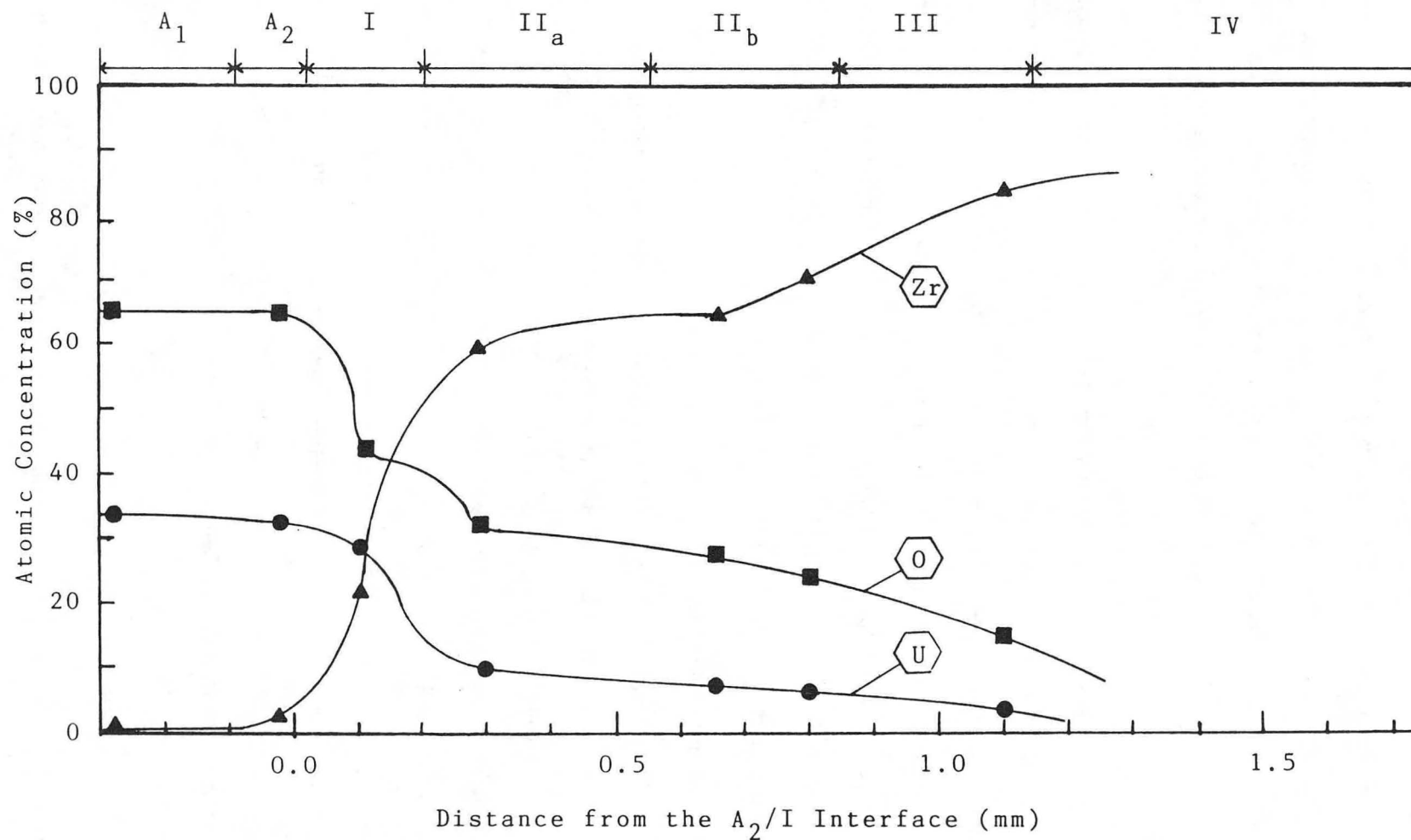


Fig. 3.13 Overall Average Concentration Variation for the UO_2 /pure Zry System from AES.
($T=2100^\circ\text{C}$, $t=30\text{ s}$)

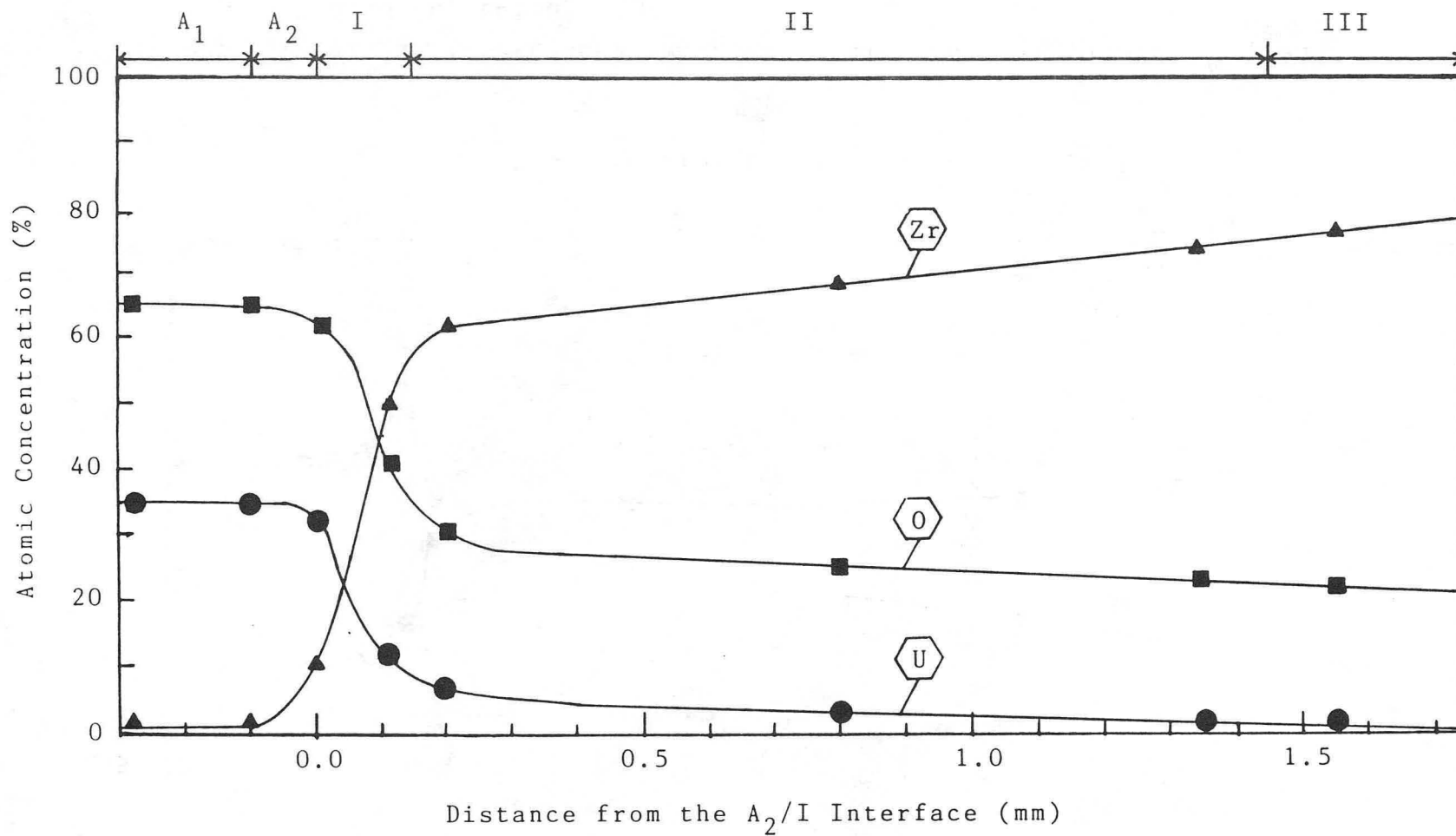


Fig.3.14 Overall Average Concentration Variation for the $\text{UO}_2/2.4\text{w/o O-Zry}$ System from AES.
($T=2100^\circ\text{C}$, $t=120\text{ s}$)

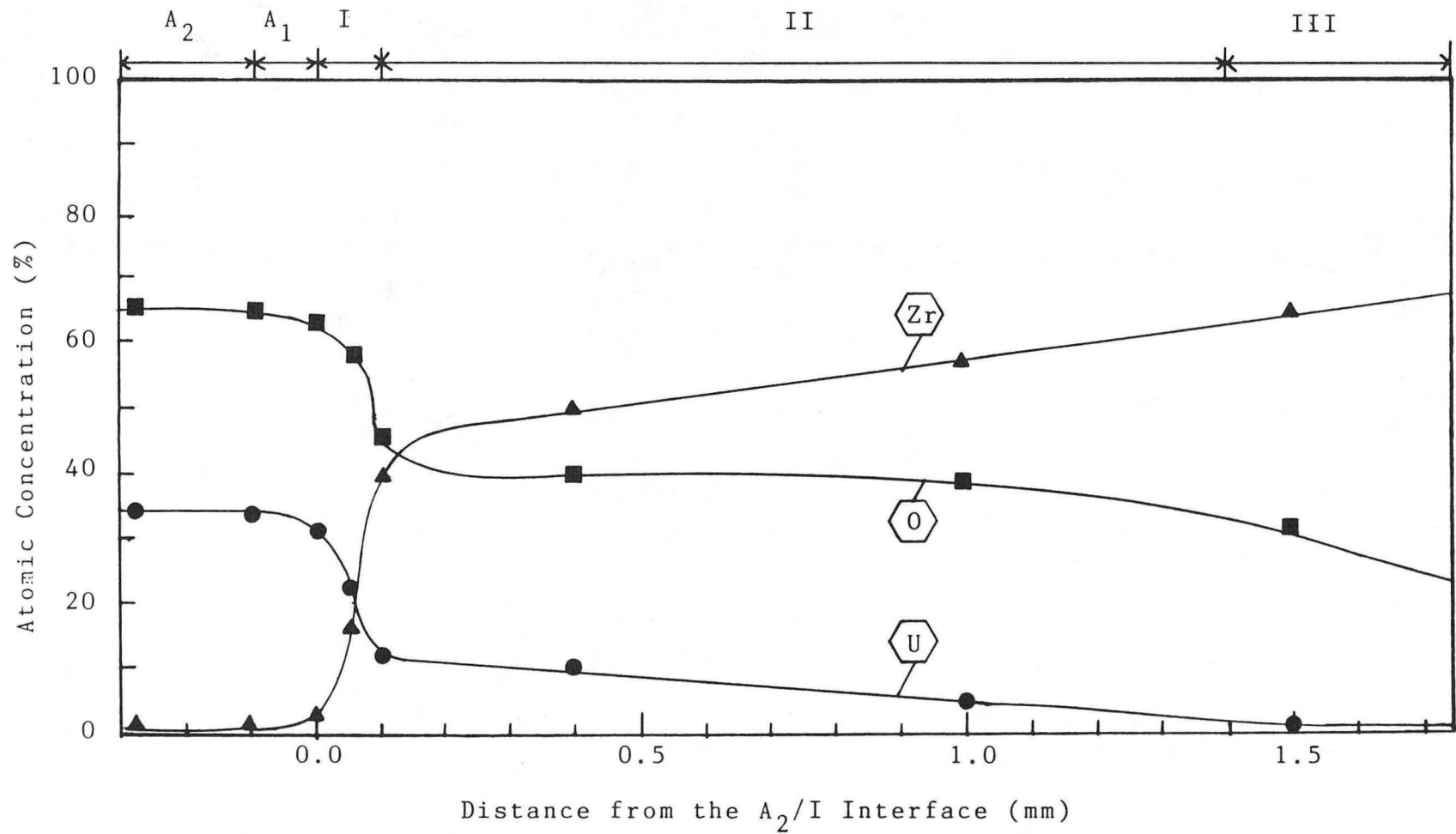


Fig. 3.15 Overall Average Concentration Variation for the $\text{UO}_2/5.0\text{w/o O-Zry}$ System from AES.
($T=2100^\circ\text{C}$, $t=150\text{ s}$)

U-Zr-O Isothermal Section at 2000 °C

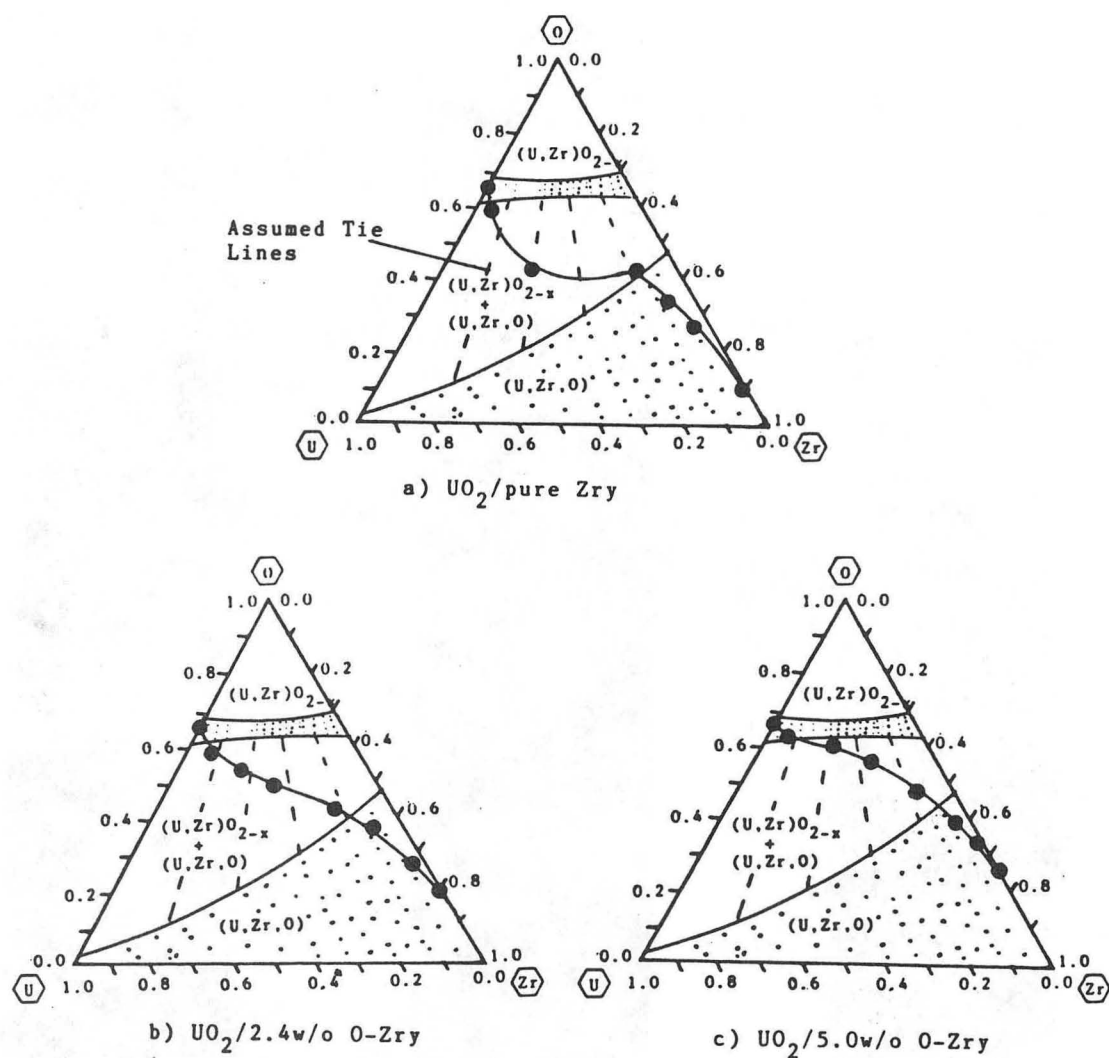


Fig. 3.16 Diffusion Paths(Solid Line and Points) on the U-Zr-O System.

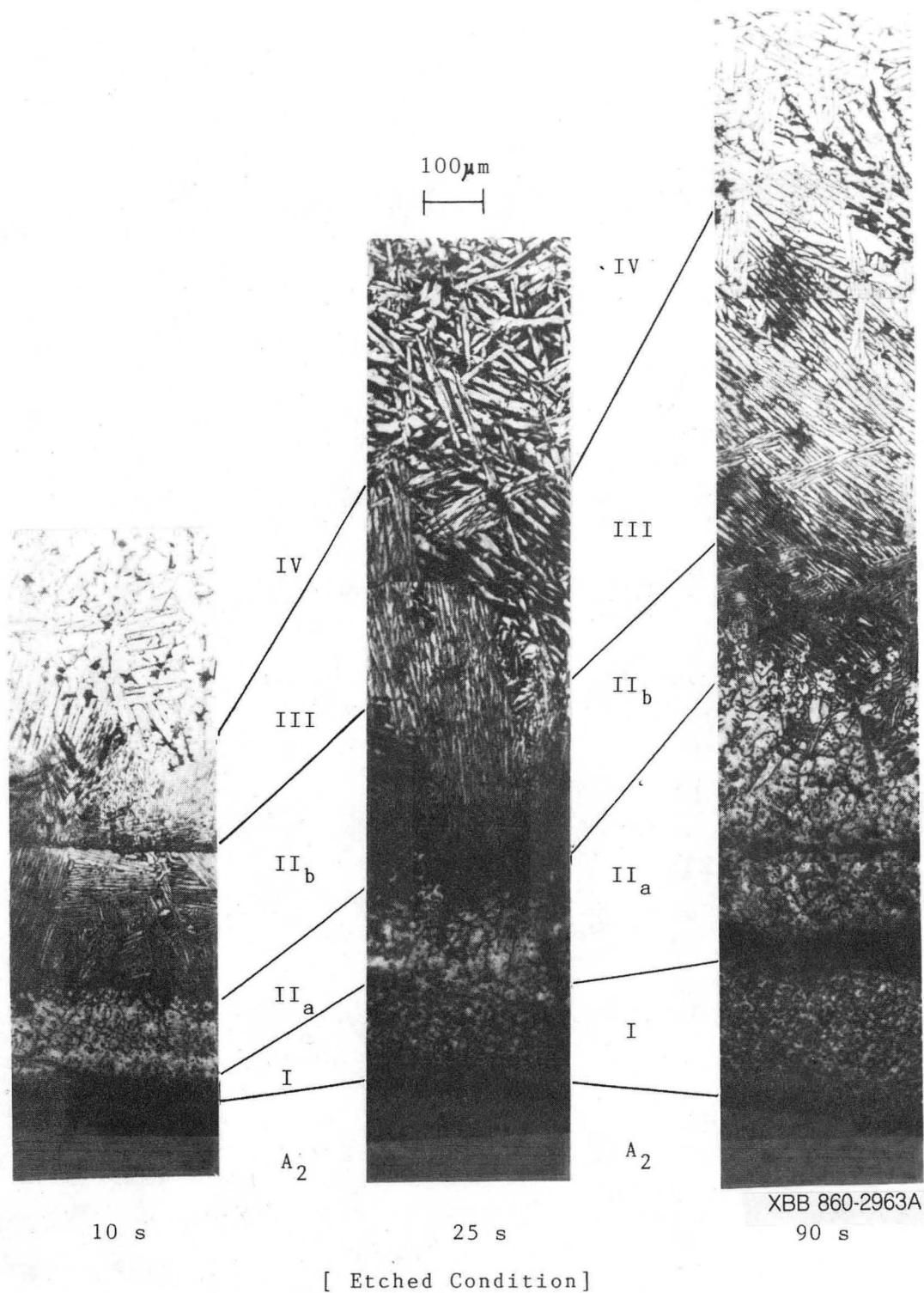


Fig. 3.17 UO_2 /pure Zry Reaction Layer Appearance as a Function of Reaction Time (Optical Photomicrograph).
($T=2000^\circ\text{C}$)

The individual reaction zone thicknesses were measured directly with an optical microscope or from the SEM micrographs or the optical photomicrographs. For the pure Zry system, etched specimens were used for the identification of region III.

For the pure Zry system, X_1 is defined as the thickness of region I, X_2 as the thickness of region II_a plus that of region II_b and X_3 as the thickness of region III. For the 2.4w/o O-Zry system, Y_1 is defined as the thickness of region I and Y_2 as the thickness of region II. For the 5.0w/o O-Zry system, Z_1 is defined as the thickness of region I and Z_2 as the thickness of region II.

The reaction zone thicknesses are plotted versus the square root of time at the various reaction temperatures in Figs. A.1 through A.10.

Comparison of the original thickness of the UO_2 disk with its thickness after reaction gives the amount of UO_2 dissolved. In the UO_2 disk/molten Zry reaction, uranium dissolution is not a clear-cut matter. Region I contains uranium which is partially dissolved in the sense that it is no longer part of the solid oxide structure; however, it has as yet been totally liquefied and incorporated into the U-Zr-O melt. In the following discussion, undissolved uranium will be considered to be that in regions A₁ and A₂, and the remainder in region I to be dissolved. The decreases of the UO_2 disk thicknesses are represented by ΔL_x , ΔL_y and ΔL_z for the pure Zry, the 2.4w/o O-Zry and the 5.0w/o O-Zry, respectively (see Figs. A.1, A.5 and A.8). These results are shown in Figs. A.11 through A.13.

The linear slopes obtained using the least square method show that the interaction between UO_2 and molten Zry is diffusion-controlled. The reaction zones growth rates are plotted versus reciprocal temperature in Arrhenius fashion in Figs. A.14 through 16. In addition, the parabolic rate constants for the UO_2 disk thickness decrease are shown in Fig. A.17. In order to determine activation energies, the least square method was used. The results are :

For the UO_2 /pure Zry reaction,

$$X_1^2/t = 5.8 \times 10^{-4} \exp(-19 \pm 7/RT)$$

$$X_2^2/t = 2.1 \times 10^1 \exp(-57 \pm 11/RT)$$

$$X_3^2/t = 1.3 \times 10^{-1} \exp(-38 \pm 6/RT)$$

$$\Delta L_x^2/t = 4.3 \times 10^{-1} \exp(-44 \pm 8/RT)$$

For the UO_2 /2.4w/o O-Zry reactions,

$$Y_1^2/t = 3.7 \times 10^{-5} \exp(-13 \pm 6/RT)$$

$$Y_2^2/t = 2.9 \times 10^1 \exp(-60 \pm 13/RT)$$

$$\Delta L_y^2/t = 2.3 \times 10^1 \exp(-65 \pm 11/RT)$$

For the UO_2 /5.0w/o O-Zry reactions,

$$Z_1^2/t = 1.3 \times 10^{-6} \exp(-4 \pm 2/RT)$$

$$Z_2^2/t = 2.1 \exp(-58 \pm 10/RT)$$

$$\Delta L_z^2/t = 2.3 \times 10^3 \exp(-88 \pm 14/RT)$$

where growth rate coefficients (X^2/t , Y^2/t and Z^2/t) are in cm^2/s , R is 1.987×10^{-3} kcal/mole K, T is in K and activation energies are in kcal/mole.

3.2 UO_2 Single Crystal/Molten Zry Reaction

3.2.1 Reaction Layers and Products

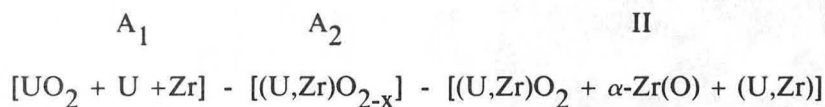
Optical photomicrographs were examined in the as-polished and the air-oxidized specimens, respectively. The layer structure near the interface was examined along a sphere radius 45 degrees from the axis of the crucible. A micrograph of a typical reacted specimen

is shown in Fig. 3.18. The reaction layer sequence is the same as that in the previous tests using polycrystalline UO_2 from region A_1 [$\text{UO}_2 + \text{U}$] to region II_a [$\alpha\text{-Zr(O)} + (\text{U,Zr})_a$]. However, the distinction in the microstructure between layer II_a and II_b was absent. Also, little prior $\beta\text{-Zry}$ was left between the spherical specimen and the ThO_2 crucible walls. Fig. 3.18 shows the distribution of porosity and shiny particles in regions A_1 and A_2 . In region A_1 , porosity and shiny particles are uniformly distributed and most of shiny particles are associated with pores. Following air-oxidation of the specimen, all of the shiny particles turned dark, indicating that they are uranium.

3.3 Polycrystalline UO_2 Crucible/Molten Zry Reaction

3.3.1 Reaction layers and Products

In this case, the interface was along the vertical side-wall of the UO_2 crucible, in contrast to the UO_2 disk experiment, in which it was horizontal. Optical photomicrographs were examined in the as-polished specimen. It was found that the number and the sequence of reaction layers depend on reaction temperature, reaction time and the initial oxygen content of the Zry. For a relatively high temperature, short time and low initial oxygen content of the Zry, the sequence of the individual reaction layers as observed at room temperature is :



which is shown in Fig. 3.19. This figure shows the near-interface regions following interaction of UO_2 crucible with pure Zry. The anneal was conducted for 20 s at 2100 °C. Although the specimen was not etched to reveal the grain structure, the majority of the pores in the A_1 and A_2 regions lie along grain boundaries. At the reaction temperature, these two regions were a solid phase and region II was a liquid phase.

For a relatively low temperature, long time and high initial oxygen content of the Zry(Fig. 3.20), region I was present and the sequence of the individual reaction layers as

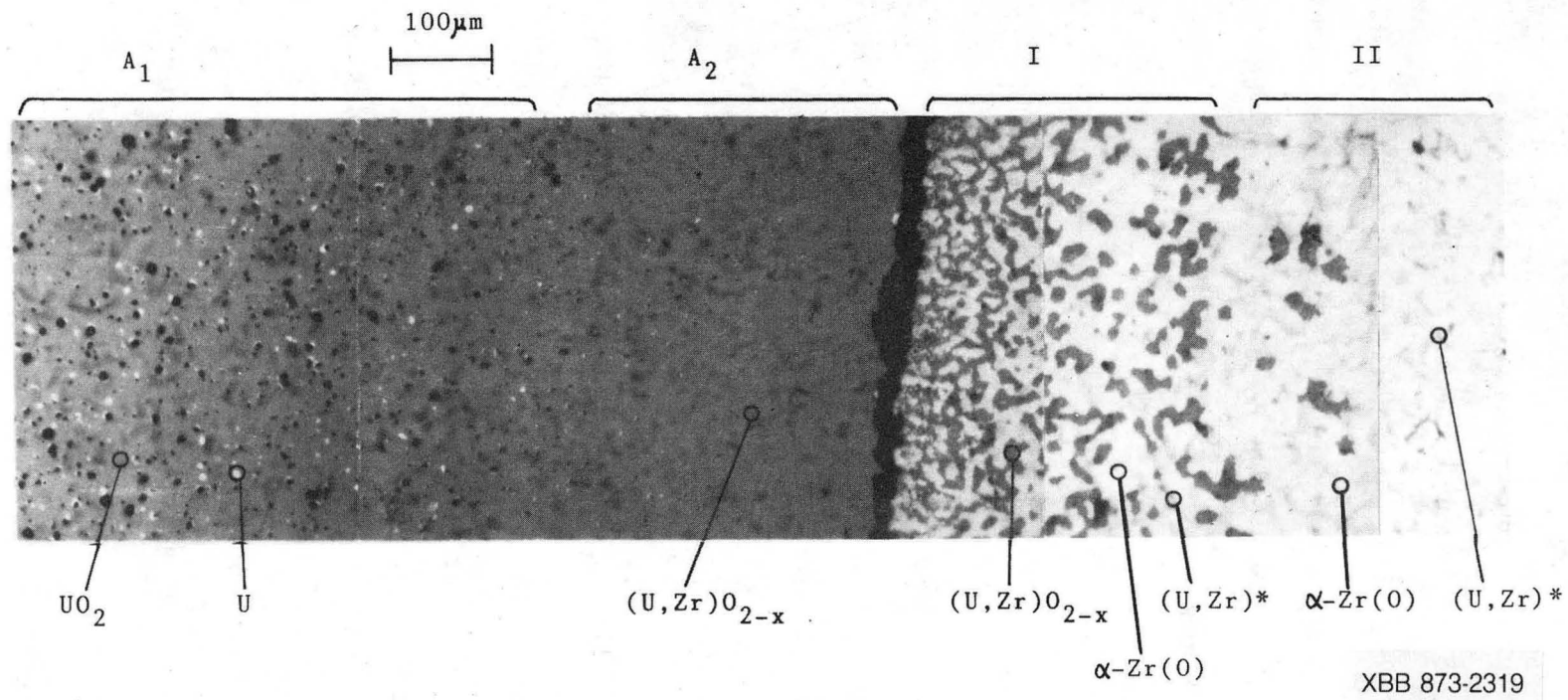


Fig. 3.18 UO_2 Single Crystal/Molten Zry Reaction Layers Appearance(Optical).
($T=2000\text{ }^\circ\text{C}$, $t=60\text{s}$)

* : The (U,Zr) phase is not visible in regions I and II ; air-oxidation is necessary to reveal this feature.

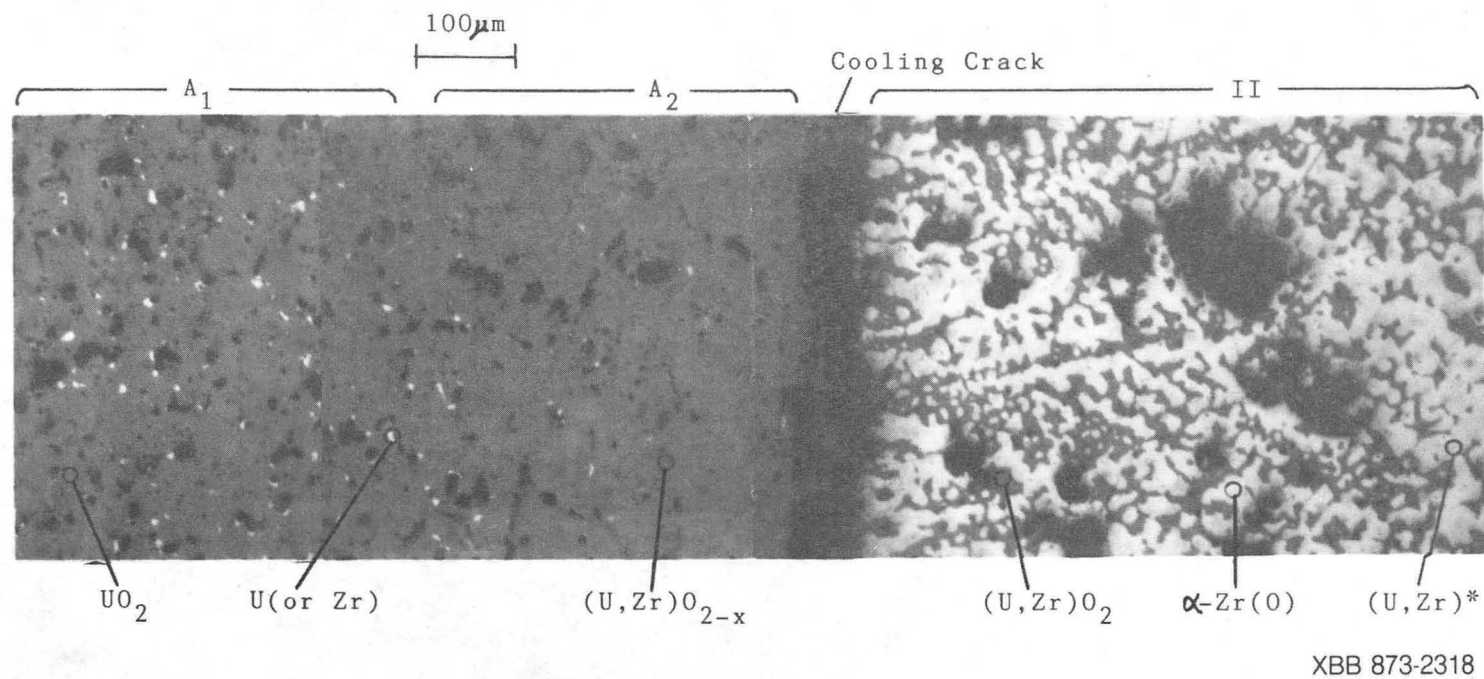


Fig.3.19 Polycrystalline UO₂ Crucible/Molten Zry Reaction Layers Appearance(Optical).
(T=2100 °C, t=20s)

* ; The (U,Zr) phase is not visible in region II ; air-oxidation is necessary to reveal this feature(see Fig. 56).

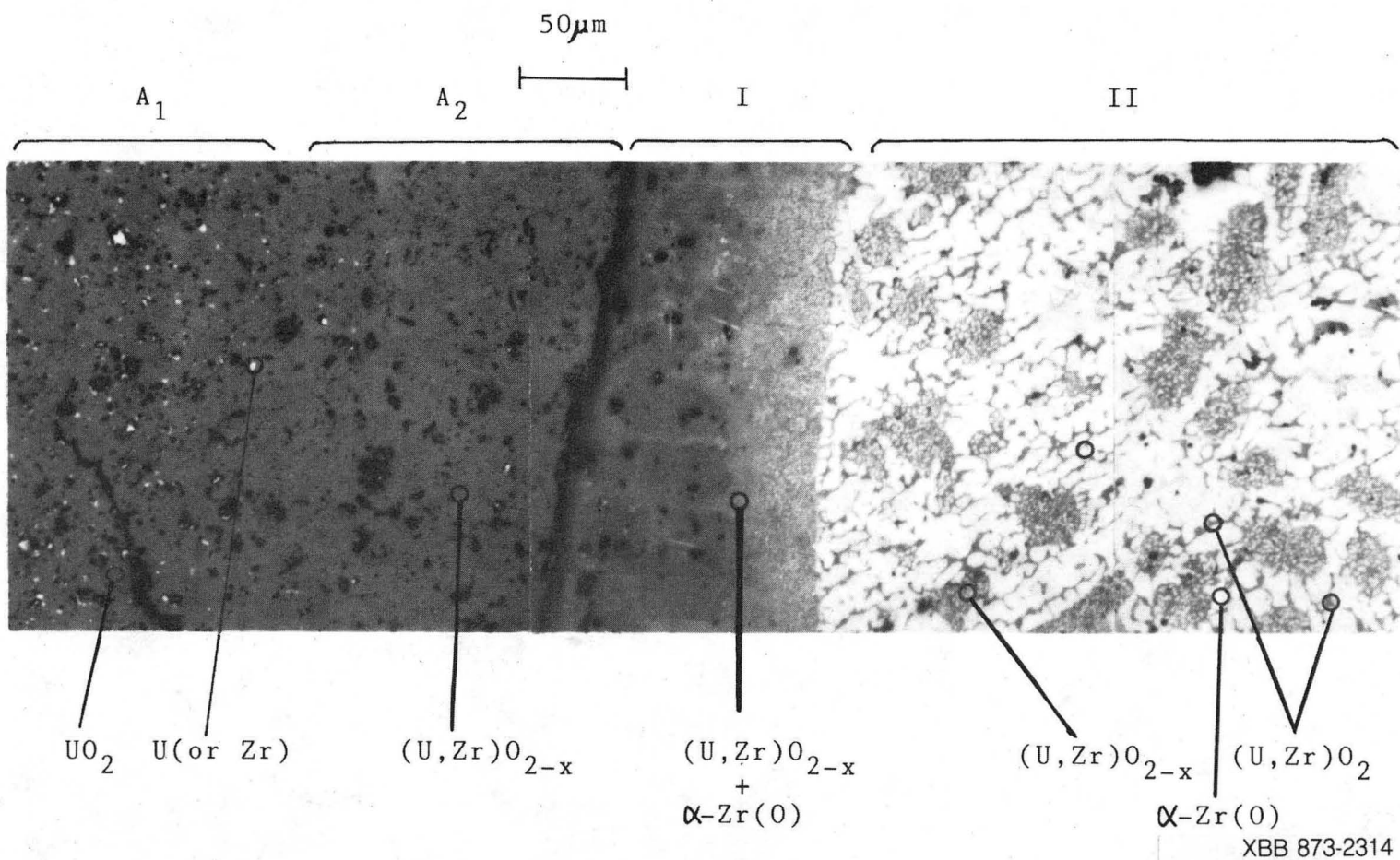
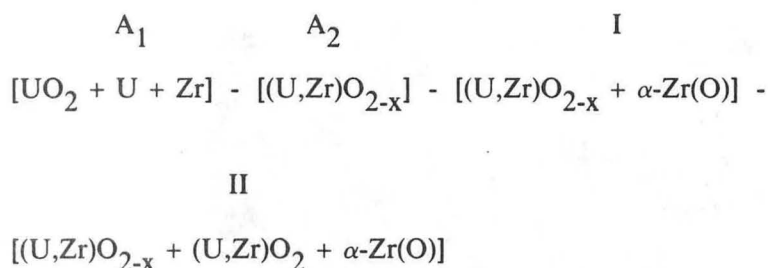


Fig. 3.20 Polycrystalline UO_2 Crucible/Molten Zry Reaction Layers Appearance(Optical).
 ($T=2000^\circ\text{C}$, $t=600\text{s}$)

observed at room temperature is :



The anneal was conducted for 600 s at 2000 °C. No (U,Zr) was formed in region II. The mixed oxide phases in region II were distinguishable microstructurally and chemically. In Fig. 3.20, the (U,Zr)O₂ phase formed thin bands in the α -Zr(O) matrix, while the (U,Zr)O_{2-x} exhibited a chunky appearance. The EMP analysis (Table 5) showed the former phase to be stoichiometric (O/M=2) and the latter hypostoichiometric (O/M=1.8). In addition, Fig. 3.21 shows (U,Zr)O_{2-x} particles in the process of becoming separated from region I and dispersed into region II. It is, therefore, believed that the (U,Zr)O₂ phase in region II precipitates from the (U,Zr,O) melt during cooling and the (U,Zr)O_{2-x} phase in region II originated from region I and existed at the reaction temperature. At the reaction temperature, regions A₁ and A₂ were a solid phase and regions I and II were a mixture of a solid phase and a liquid phase.

The appearances of regions A₁ and A₂ are exactly same as those for the polycrystalline UO₂ disk/molten Zry system. Fig. 3.22 shows that porosity and shiny particles are uniformly distributed in region A₁. Moreover, they are present throughout the entire thickness of the UO₂ crucible wall. In addition, Fig. 3.23 shows that the porosity and the concentration of shiny particles in region A₁ increase as reaction temperature increases and Fig. 3.24 shows that they are independent of reaction times greater than ~60 s.

Fig. 3.25 shows the microstructure of region I. This figure shows that the porous-medium-like structure is apparent near the A₂/I interface and changes to the channel structure mixed with the porous-medium-like structure on moving radially inward (towards the right in the photomicrograph). This figure also shows that region I has no (U,Zr) channels,

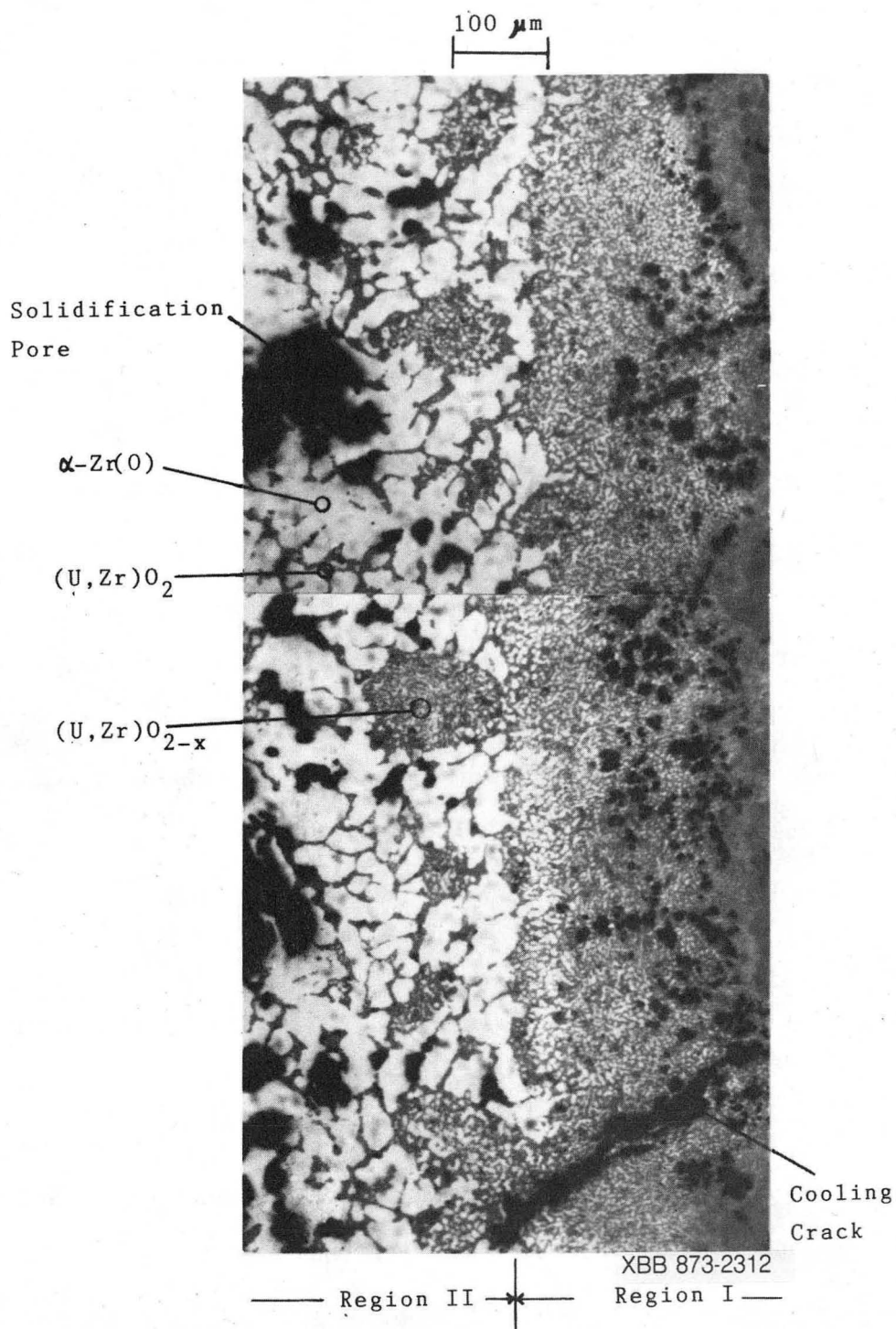


Fig. 3.21 Sweeping of $(\text{U,Zr})\text{O}_{2-x}$ Particles by the Convective Motion of the Melt. ($T=2000\text{ }^{\circ}\text{C}$, $t=1200\text{ s}$)

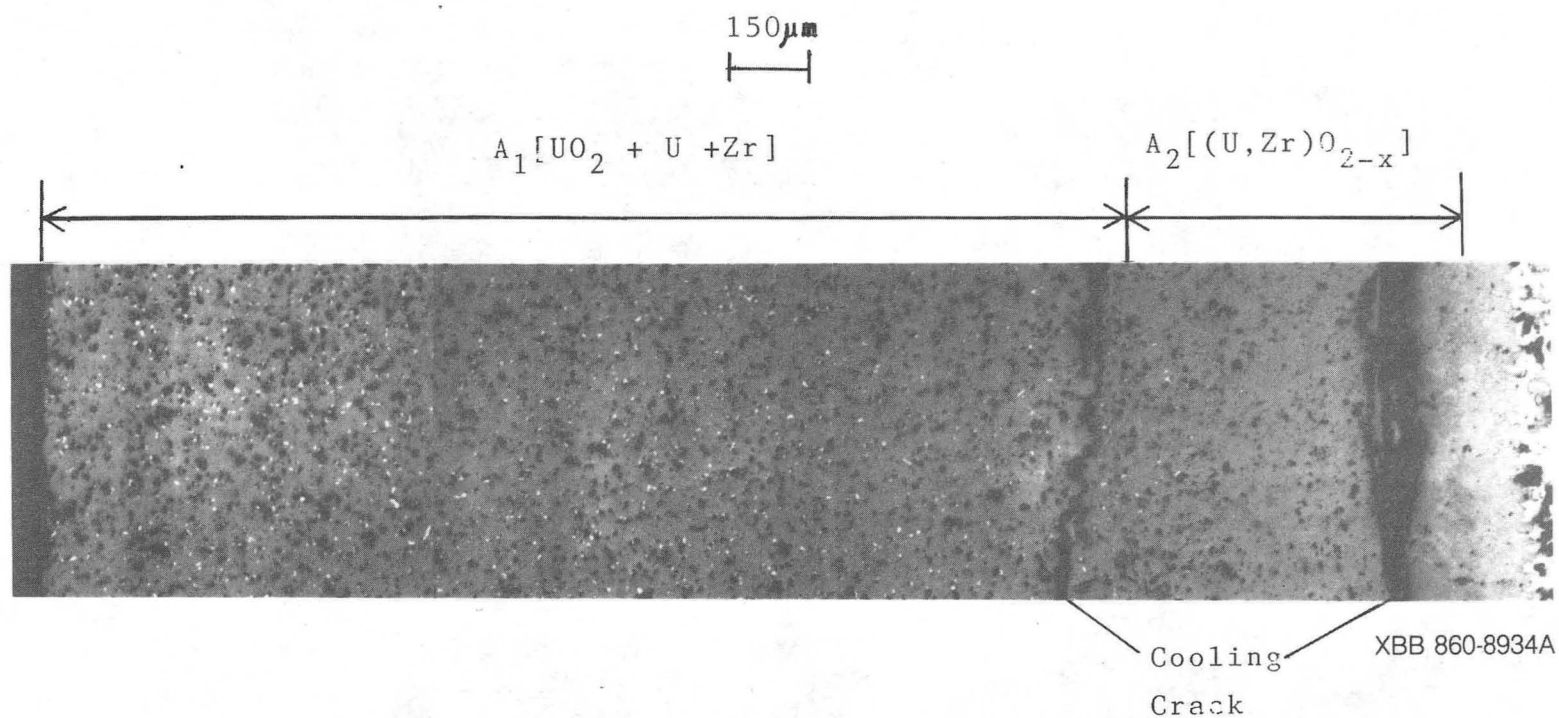


Fig.3.22 Microstructural Appearance of Region A_1 and A_2 for UO_2 Crucible/Molten Zry System(Optical). ($T=2000\text{ }^\circ\text{C}$, $t=420\text{ s}$)

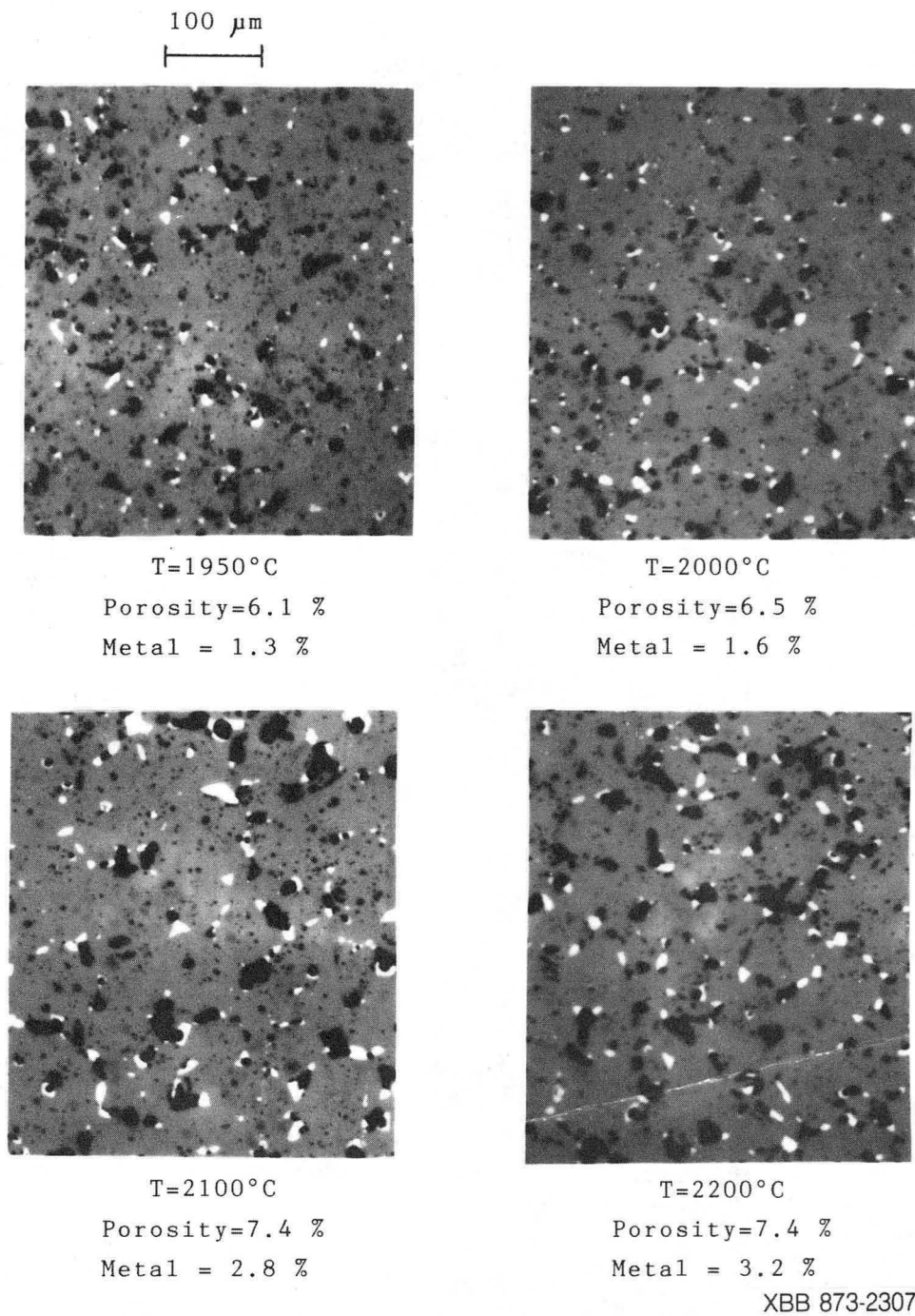


Fig. 3.23 Microstructure of Region A₁ for the UO₂ Crucible / Molten Zry System as a Function of Reaction Temperature (t=120 s).

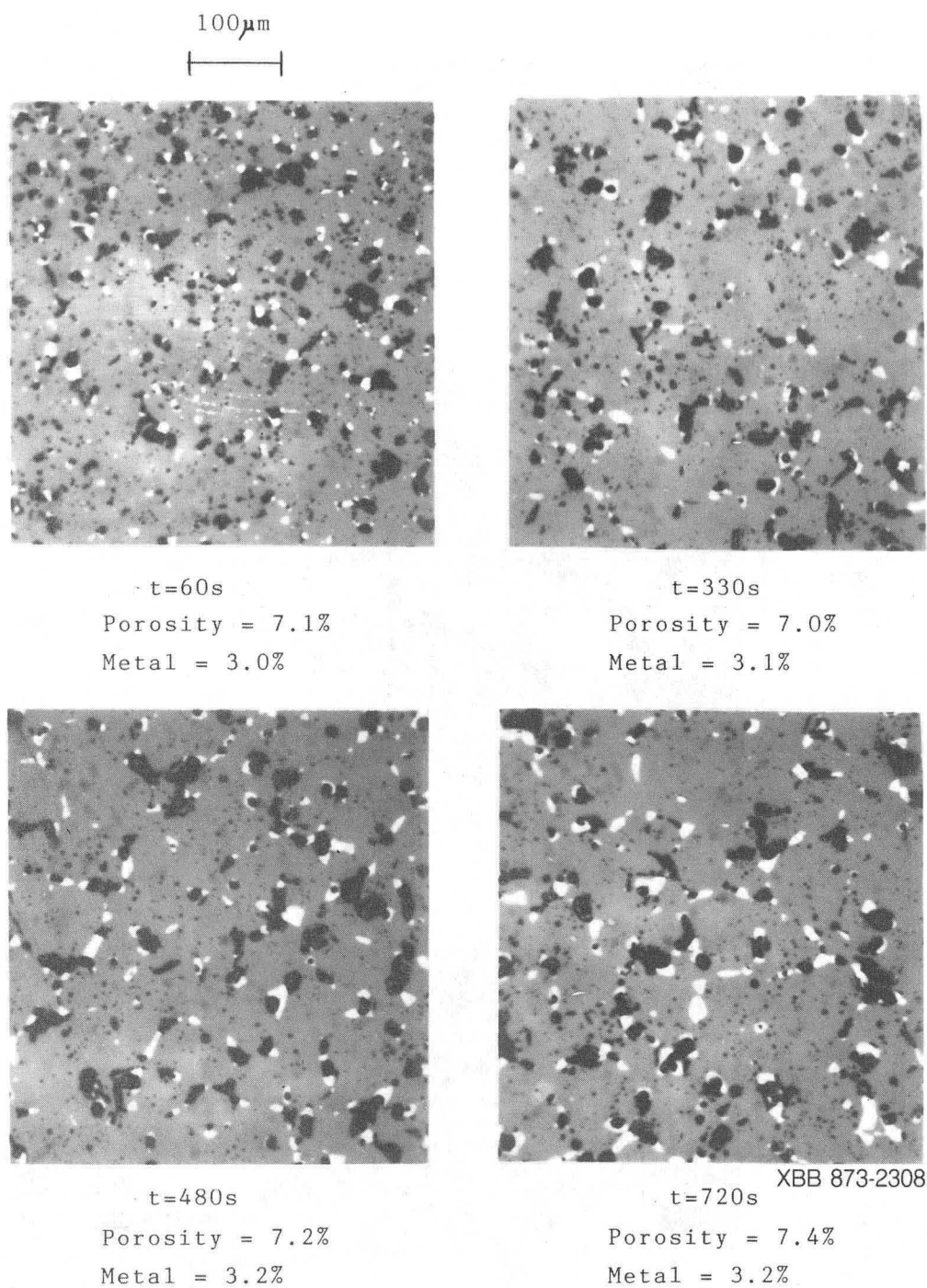


Fig. 3.24 Microstructure of Region A₁ for the UO₂ Crucible /Molten Zry System as a Function of Reaction Time. (T=2200°C)

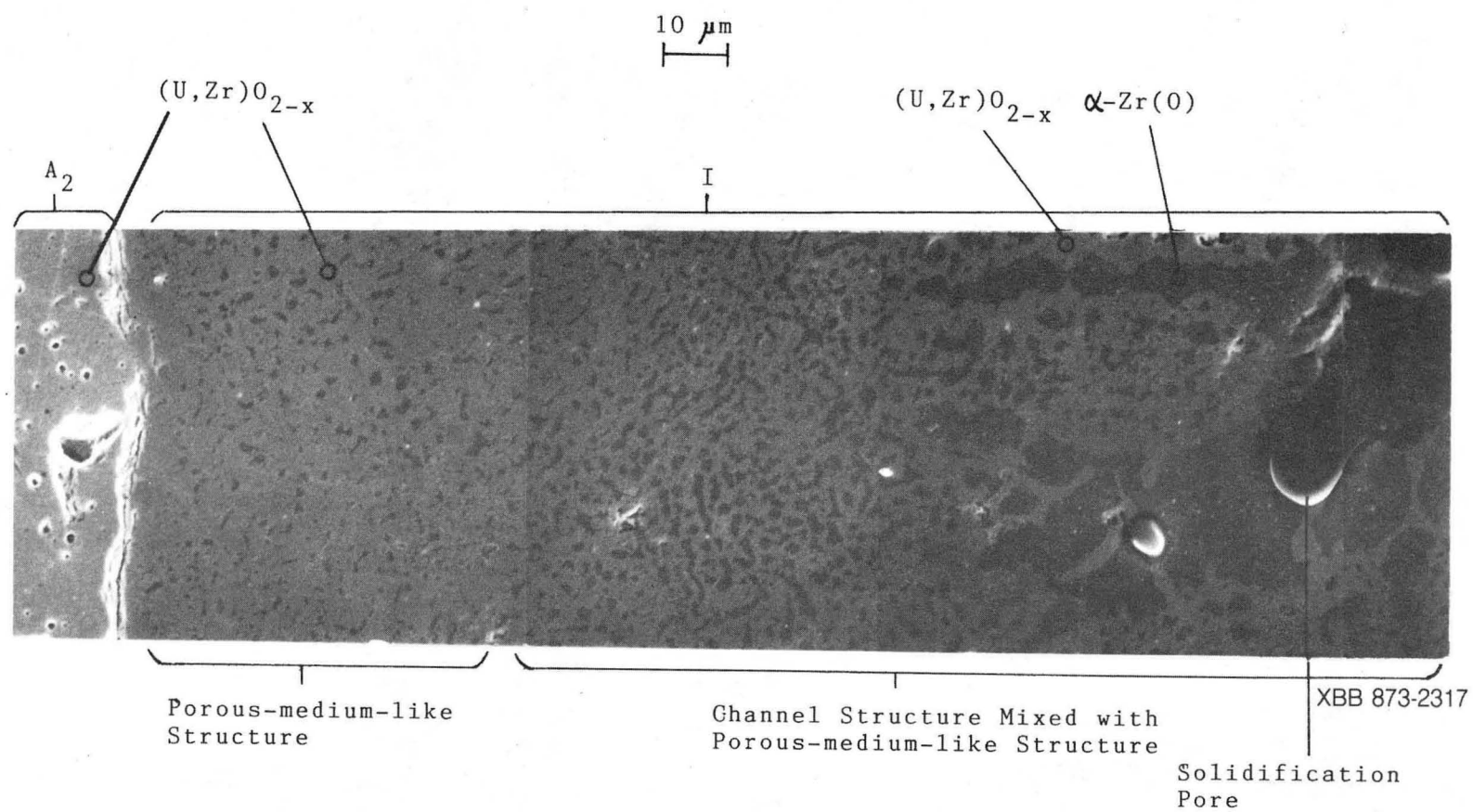


Fig. 3.25 Microstructure of Region I for the UO_2 Crucible/Molten Zry System(SEM).
($T=2000^\circ\text{C}$, $t=600\text{ s}$)

which indicates a high oxygen content of the (U,Zr,O) melt. This is consistent with the results of the UO_2 disk/5.0w/o O-Zry system(see Fig. 3.11).

The microstructures of region II, which occupies the entire central portion of the crucible, are shown in Figs. 3.26 through 3.30 as a function of reaction time and temperature for the reaction with pure Zry. From these figures, it was found that region II is composed of $\alpha\text{-Zr(O)}$, (U,Zr) and $(\text{U,Zr})\text{O}_2$ for a relatively short reaction time and of $\alpha\text{-Zr(O)}$, $(\text{U,Zr})\text{O}_2$ and $(\text{U,Zr})\text{O}_{2-x}$ for a relatively long reaction time. Fig. 3.31 shows comparable microstructures for the reaction with 6w/o O-Zry. From this figure, it was found that region II is composed of $\alpha\text{-Zr(O)}$, $(\text{U,Zr})\text{O}_2$ and $(\text{U,Zr})\text{O}_{2-x}$, regardless of reaction time. Figs. 3.26 through 3.31 show that the porosity in region II becomes larger as reaction time increases. This porosity is probably due to shrinkage during the solidification process ; the uranium concentration in the Zry melt increases with an increase of reaction time, thus causing more U-rich (U,Zr) alloys to form during the solidification process. Note that the density of uranium is approximately a factor-of-three higher than that of zirconium.

3.3.2 Elemental Concentration Distribution

The U, Zr, O concentrations of the individual reaction product phases in regions I and II were determined by EMP. The results are shown in Table 5. The overall average concentrations scanned perpendicular to the reaction interface were determined from the AES analysis. The results are shown in Figs. 3.32 and 3.33. The boundaries of the microstructural regions determined by metallographic examination are also shown.

Figs. 3.32 and 33 show that there is no concentration gradient in region II suggesting that this region was liquid at reaction temperature. The compositions of $(\text{U,Zr})\text{O}_2$ and $\alpha\text{-Zr(O)}$ phases in region II are independent of reaction time. The $(\text{U,Zr})\text{O}_2$ contains about 63 w/o Zr and 24 w/o oxygen. The $\alpha\text{-Zr(O)}$ contains 5 w/o U and 6 w/o oxygen. The composition of $(\text{U,Zr})\text{O}_{2-x}$ phase in region II is nearly constant and is about 35w/o Zr and 15w/o oxygen. The (U,Zr) phase in region II contains no oxygen.

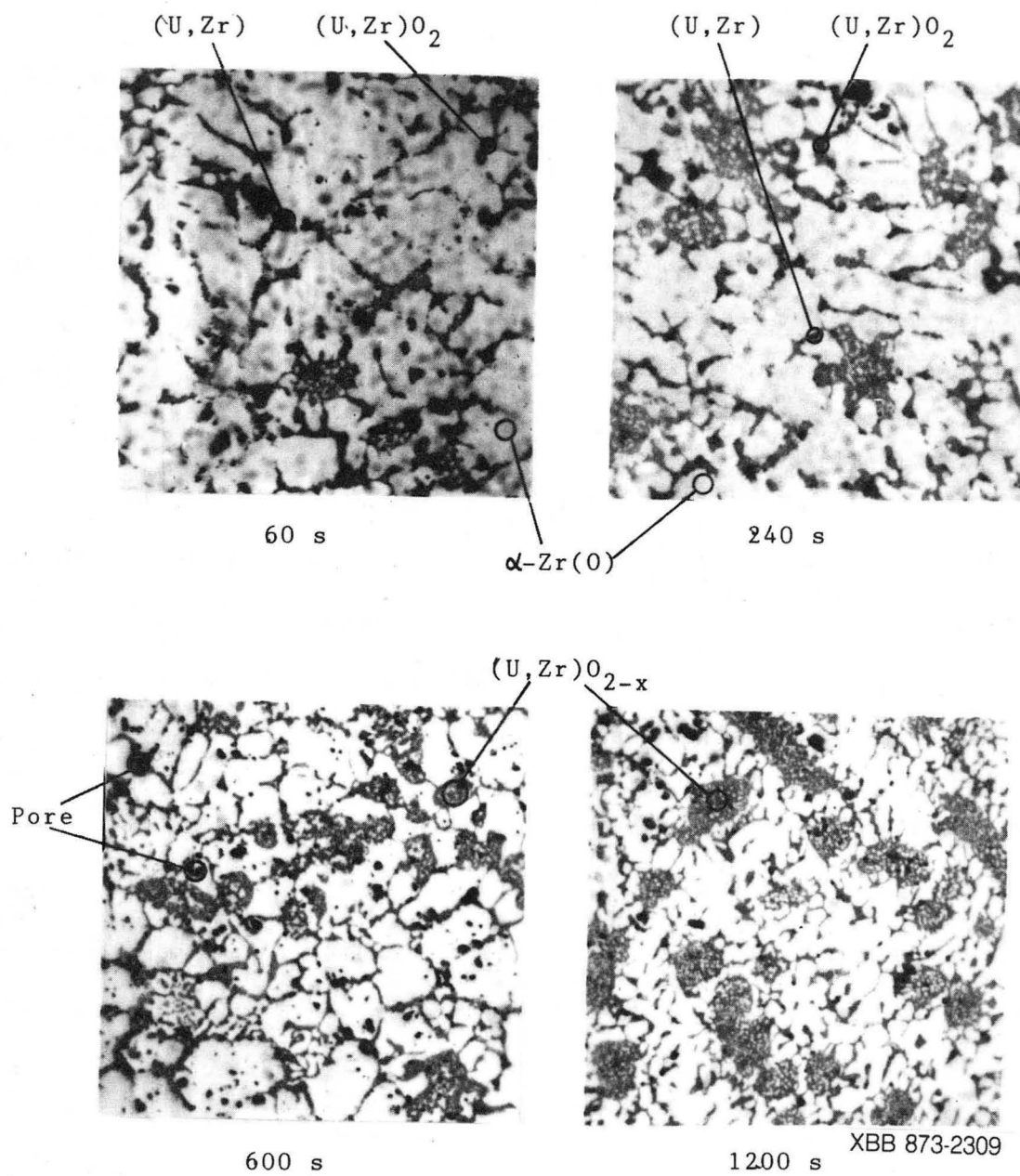


Fig.3.26 Microstructure of Region II for Polycrystalline UO_2 Crucible/Pure Zry System as a Function of Reaction Time(Optical). ($T=1950^\circ\text{C}$)

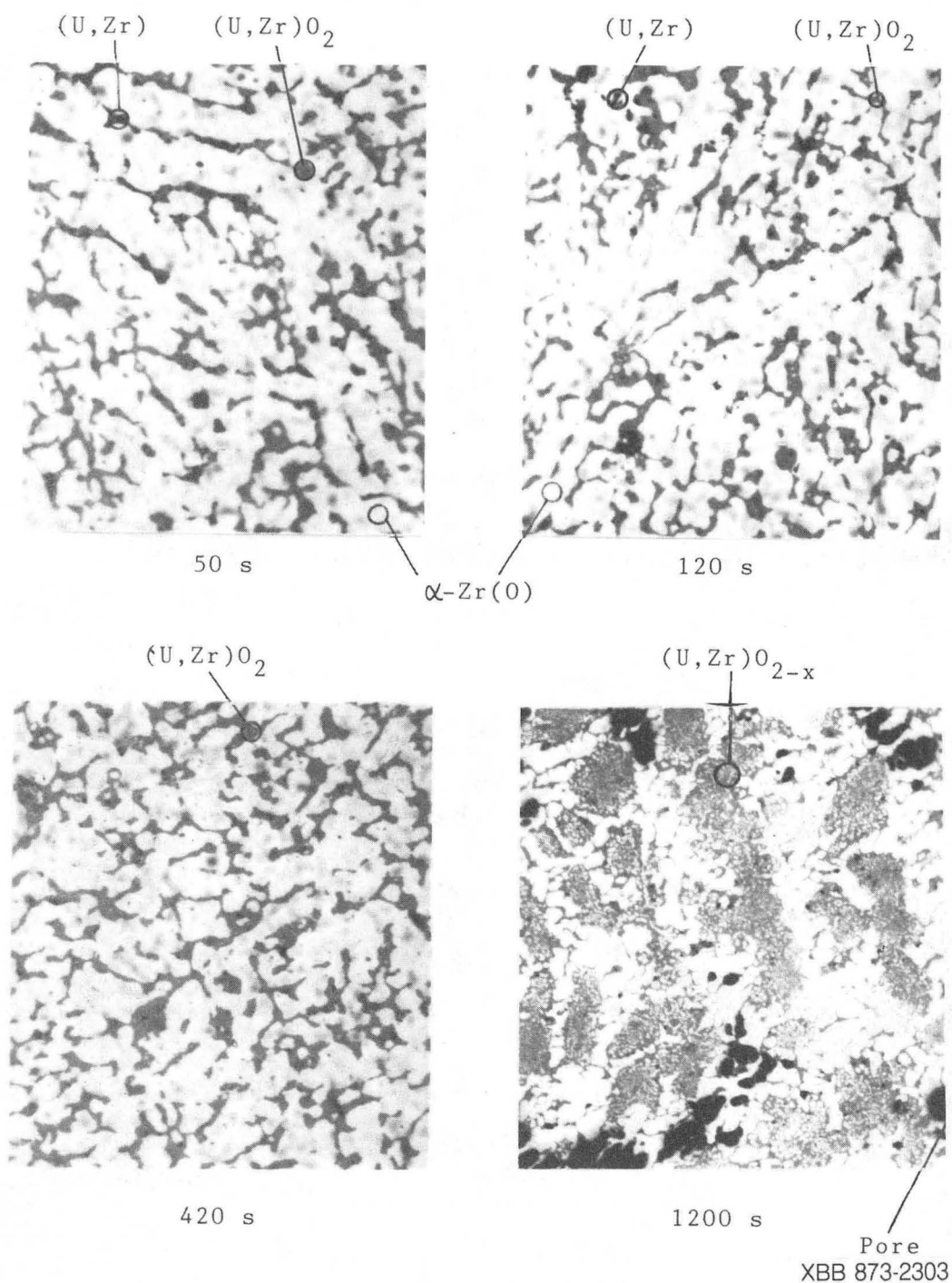


Fig. 3.27 Microstructure of Region II for Polycrystalline UO_2 Crucible/Pure Zry System as a Function of Reaction Time(Optical). ($T=2000^\circ\text{C}$)

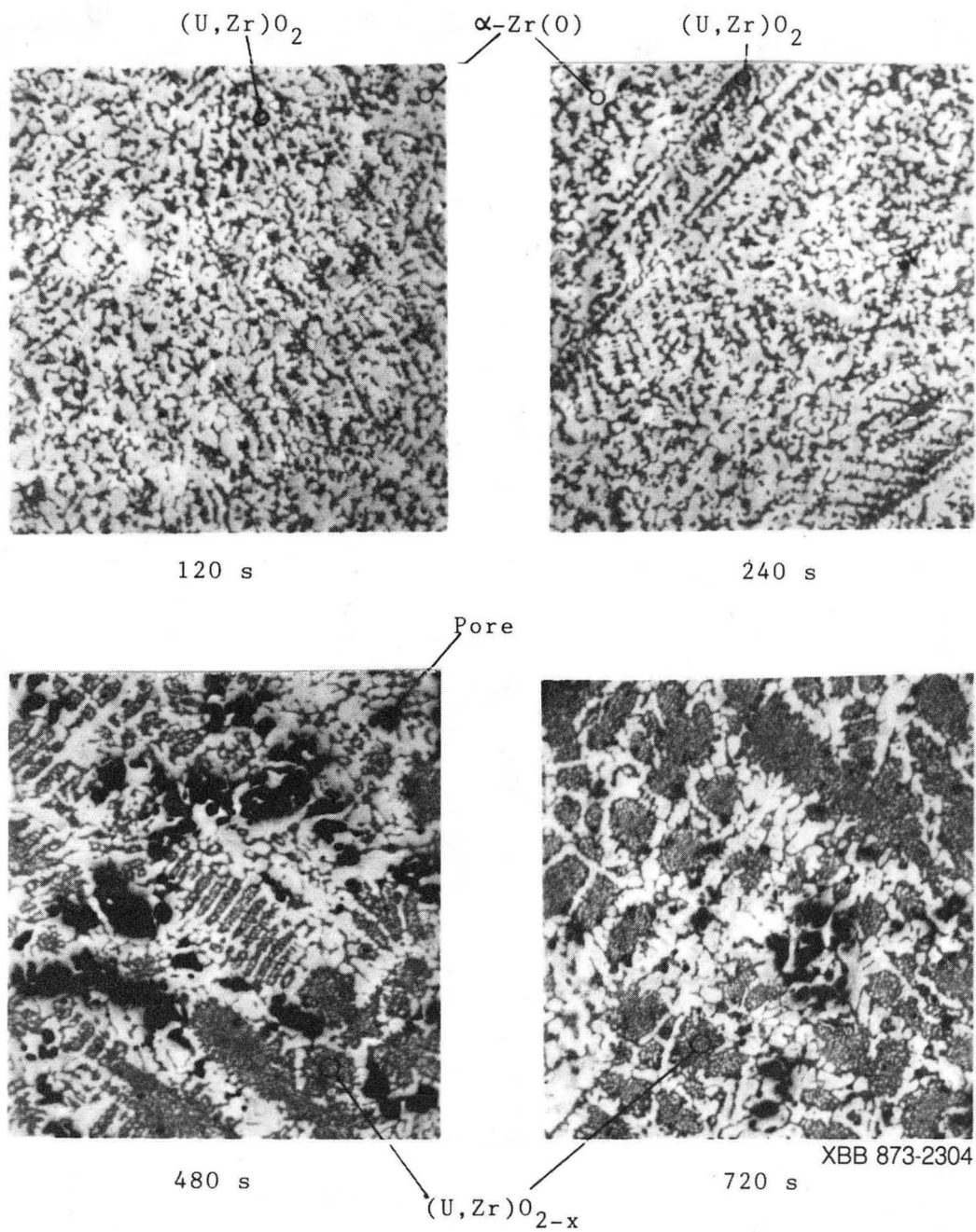


Fig. 3.28 Microstructure of Region II for Polycrystalline UO_2 Crucible/Pure Zry System as a Function of Reaction Time(Optical). ($T=2050^\circ\text{C}$)

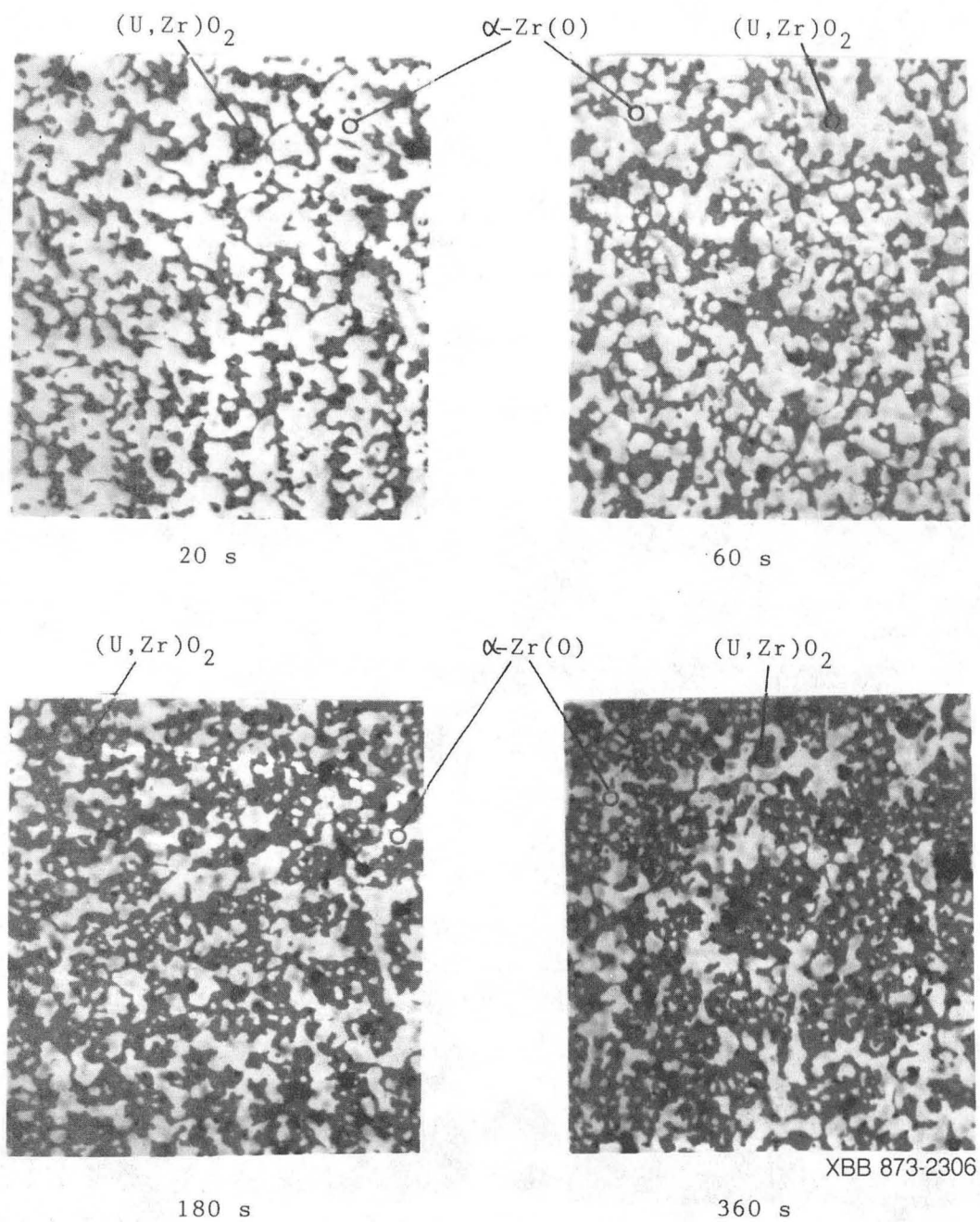


Fig. 3.29 Microstructure of Region II for Polycrystalline UO_2 Crucible/Pure Zry System as a Function of Reaction Time(Optical). ($T=2100^\circ\text{C}$)

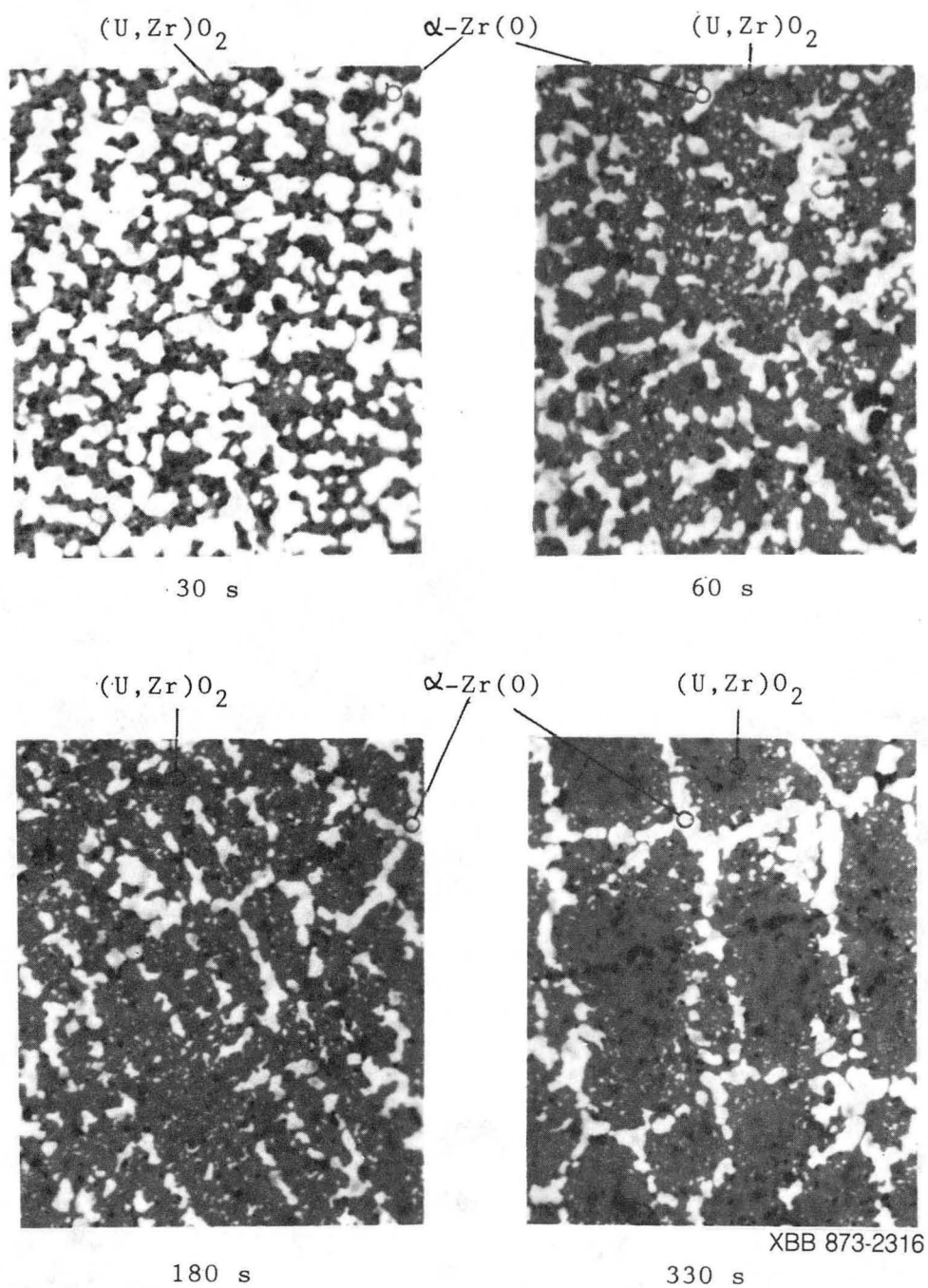


Fig. 3.30 Microstructure of Region II for Polycrystalline UO_2 Crucible/Pure Zry System as a Function of Reaction Time(Optical). ($T=2200^\circ\text{C}$)

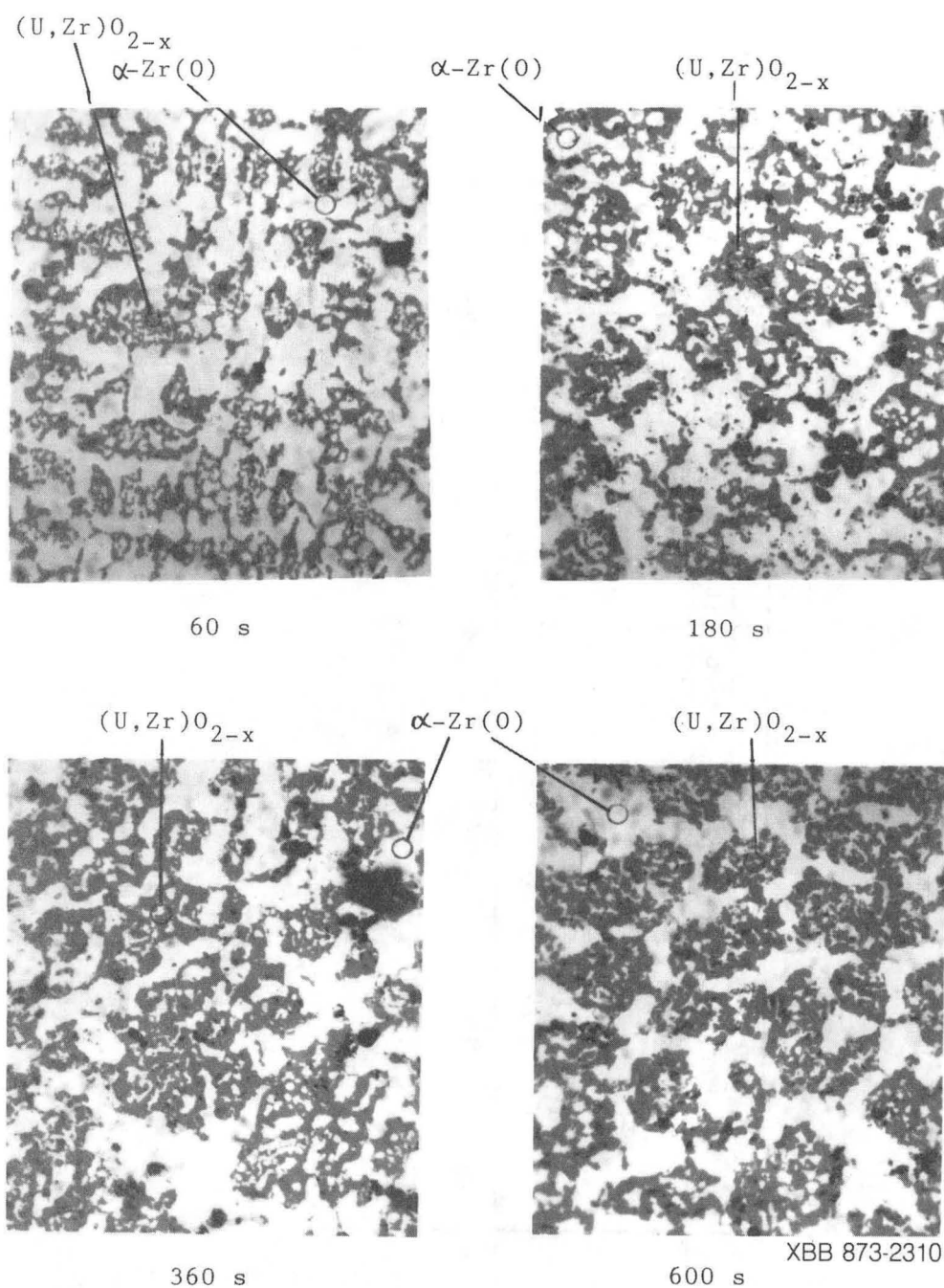


Fig. 3.31. Microstructure of Region II for Polycrystalline UO_2 Crucible/6.0w/o O-Zry System as a Function of Reaction Time(Optical). ($T=2100^\circ C$)

Table 5 Compositions for polycrystalline UO_2 crucible/pure Zry system from EMP analysis (in wt%)*

Temp. (°C)	Time (sec)	Element	Region A ₂	Region I		Region II			
			(U,Zr)O _{2-x}	(U,Zr)O _{2-x}	α -Zr(O)	(U,Zr)O _{2-x}	(U,Zr)O ₂	α -Zr(O)	(U,Zr)
2000	60	U	90	58 - 83	5 - 6		13 - 15	4 - 5	78 - 90
		Zr	**	5 - 27	87 - 88		60 - 63	90 - 91	10 - 12
		O	10	12 - 15	6		23 - 24	6	**
	600	U	90	52 - 80	5 - 6	50	13 - 15	4 - 5	
		Zr	**	8 - 30	87 - 88	35	60 - 63	90 - 91	
		O	10	12 - 17	6	15	23 - 24	6	

* Oxygen by difference [100 - (U + Zr + Sn)w/o]

** Less than the detection limit of EMP

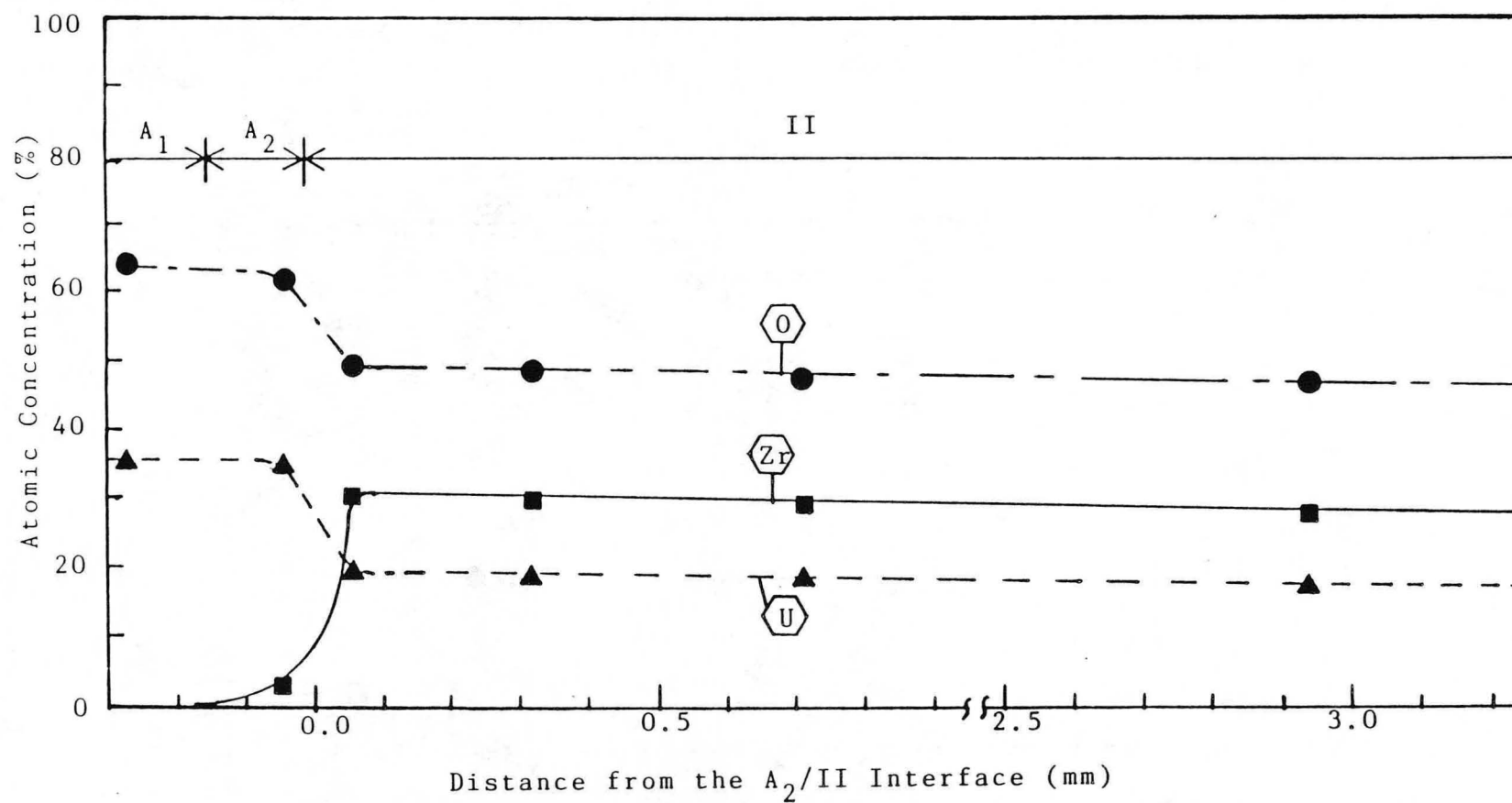


Fig.3.32 Overall Average Concentration Variation for the UO₂ Crucible/pure Zry System.
(T=2200 °C, t=60 s)

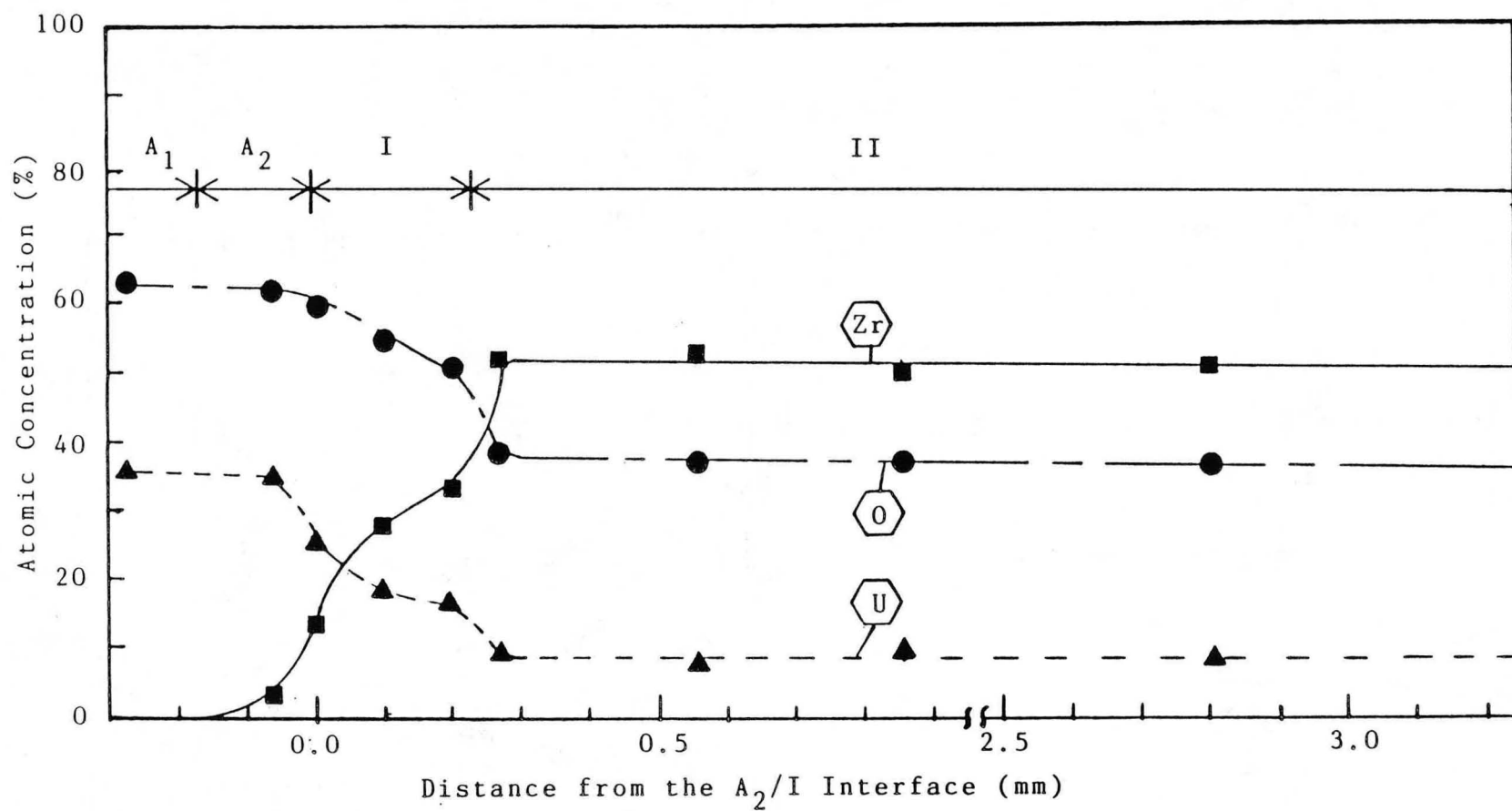


Fig.3.33 Overall Average Concentration Variation for the UO₂ Crucible/pure Zry System
(T=2000 °C, t=600 s)

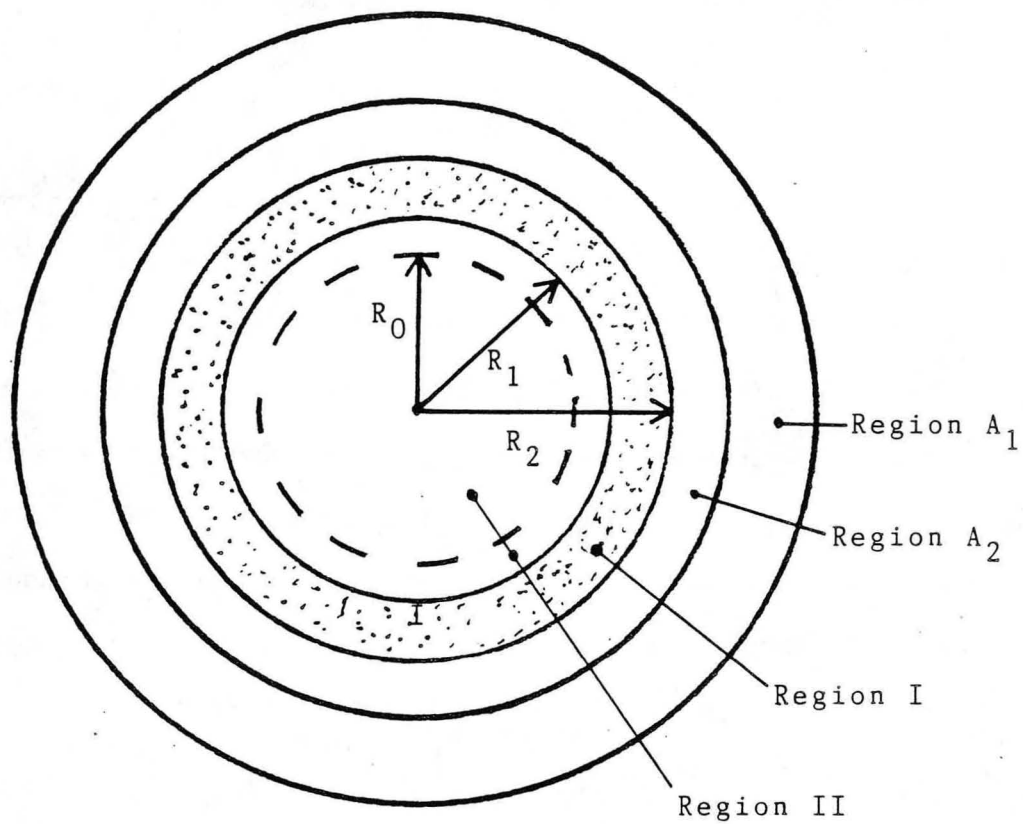
The $(\text{U,Zr})\text{O}_{2-x}$ phase in region I shows a concentration gradient. This phase contains up to 27w/o Zr and 15w/o oxygen at 2000° C for 60 s and up to 30w/o Zr and 17w/o oxygen at 2000° C for 600 s. The compositions of $\alpha\text{-Zr(O)}$ phase in region I, however, is independent of reaction time. The $\alpha\text{-Zr(O)}$ phase contains about 6 w/o U and 6 w/o oxygen.

3.3.3 Kinetics of Layer Growth and Uranium Dissolution

The extent of the layer growth for the polycrystalline UO_2 crucible/molten Zry system depends on reaction temperature, reaction time and the initial oxygen content of the Zry. Fig. 3.34 shows a schematic diagram of the UO_2 crucible/molten Zry system. R_0 is defined as the original radius of the UO_2 crucible, R_1 is the radius of the I/II interface and R_2 is the radius of the A_2/I interface. The individual radii were measured directly with an optical microscope. In Figs. 3.35 through 3.40, the radii are plotted versus the square root of time for the various reaction temperatures. Although R_1 and R_2 vary linearly when plotted against the square root of time, this behavior does not prove that reaction rate is diffusion-controlled. As will be discussed later, the kinetics are probably governed by fluid mass transfer driven by natural circulation in the melt.

These figures show that there is an incubation period for the appearance of region I. This incubation period increases as reaction temperature increases and as the initial oxygen content of the Zry decreases. After this incubation period, the I/II(R_1) and A_2/I (R_2) interfaces show parabolic kinetic behavior. UO_2 crucible/6.0w/o O-Zry system (Fig. 3.40) shows that the incubation period is quite small and that the amount of UO_2 dissolved is much smaller than that in pure Zry at the same temperature (Fig. 3.38). The difference between R_1 and R_2 gives the thickness of region I. The growths of region I at the various temperatures are plotted versus the square root of time in Fig. 3.41. From this figure, the parabolic rate constants of region I were calculated. The results are :

$$X^2 / (t - 10.6) = 5.6 \times 10^{-7} \quad \text{at } 1950^\circ \text{ C}$$



R_0 = Original Interface between UO_2 Crucible and Zry

R_1 = the I/II Interface

R_2 = the A_2 /I Interface

Fig. 3.34 A Schematic Diagram of the UO_2 Crucible/molten Zry System.

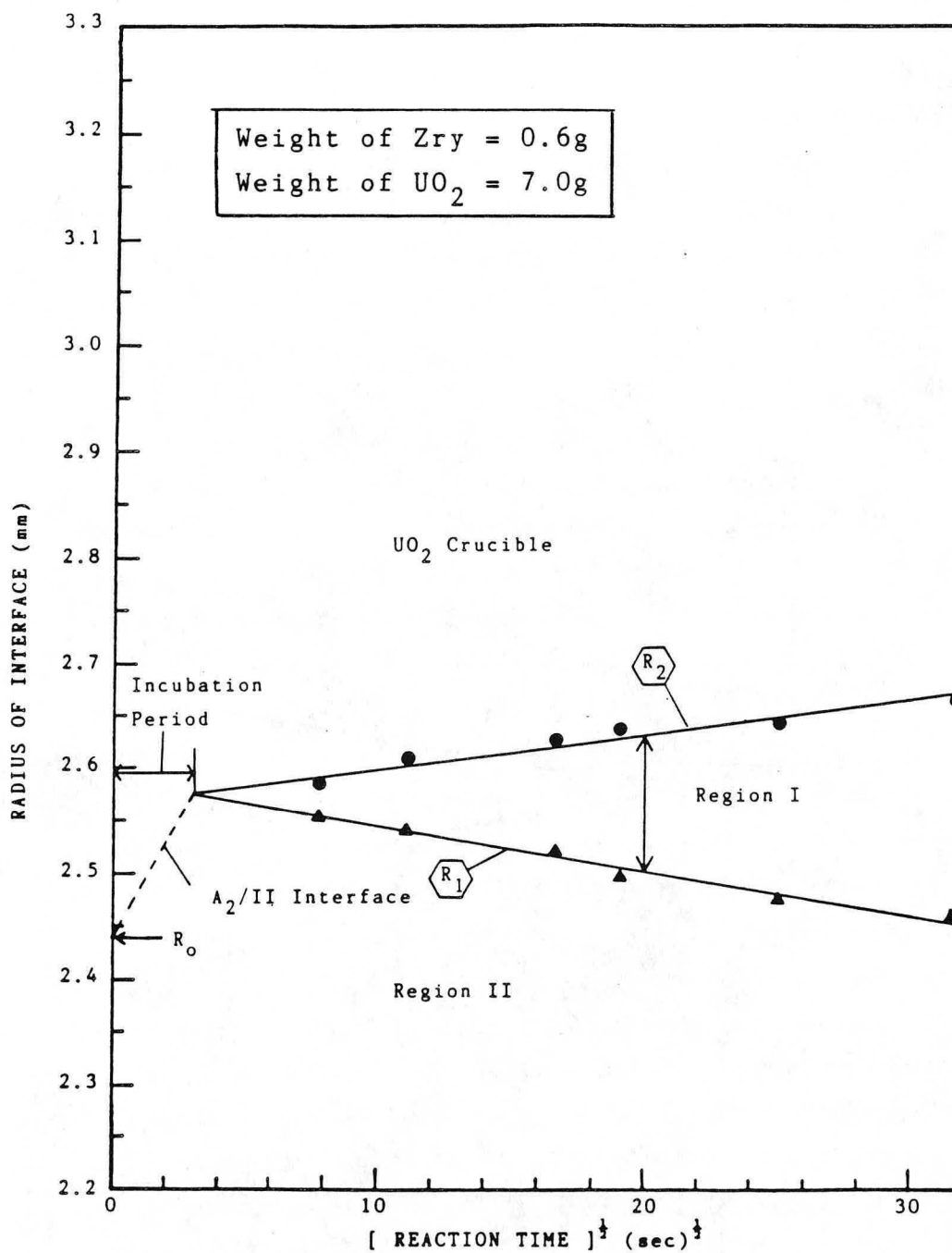


Fig.3.35 Movement of the Reaction Layers in the UO₂ Crucible/PureZry System. (T=1950 °C)

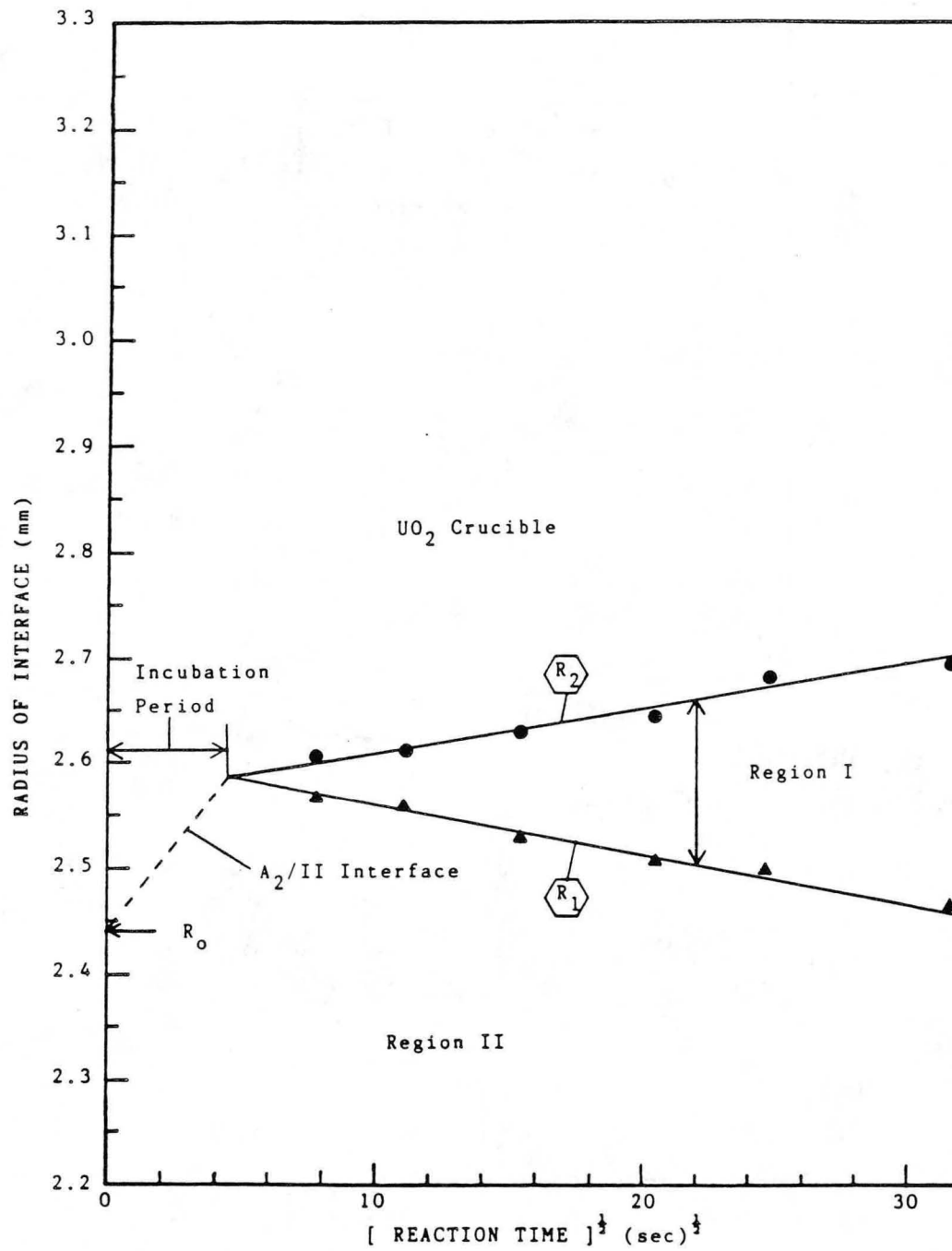


Fig. 3.36 Movement of the Reaction Layers in the UO₂ Crucible/Pure Zry System. (T=2000 °C)

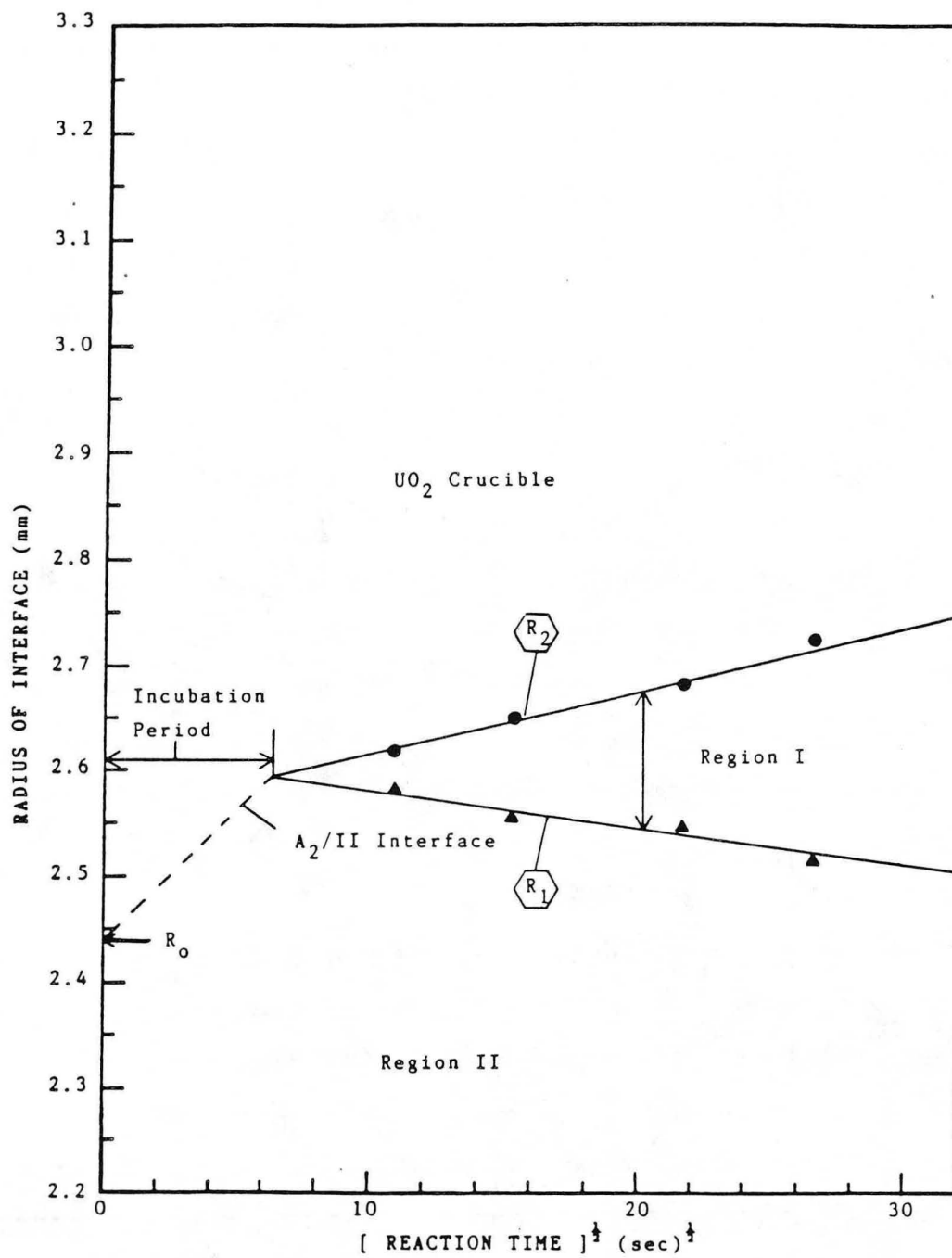


Fig.3.37 Movement of the Reaction Layers in the UO₂ Crucible/Pure Zry System. (T=2050 °C)

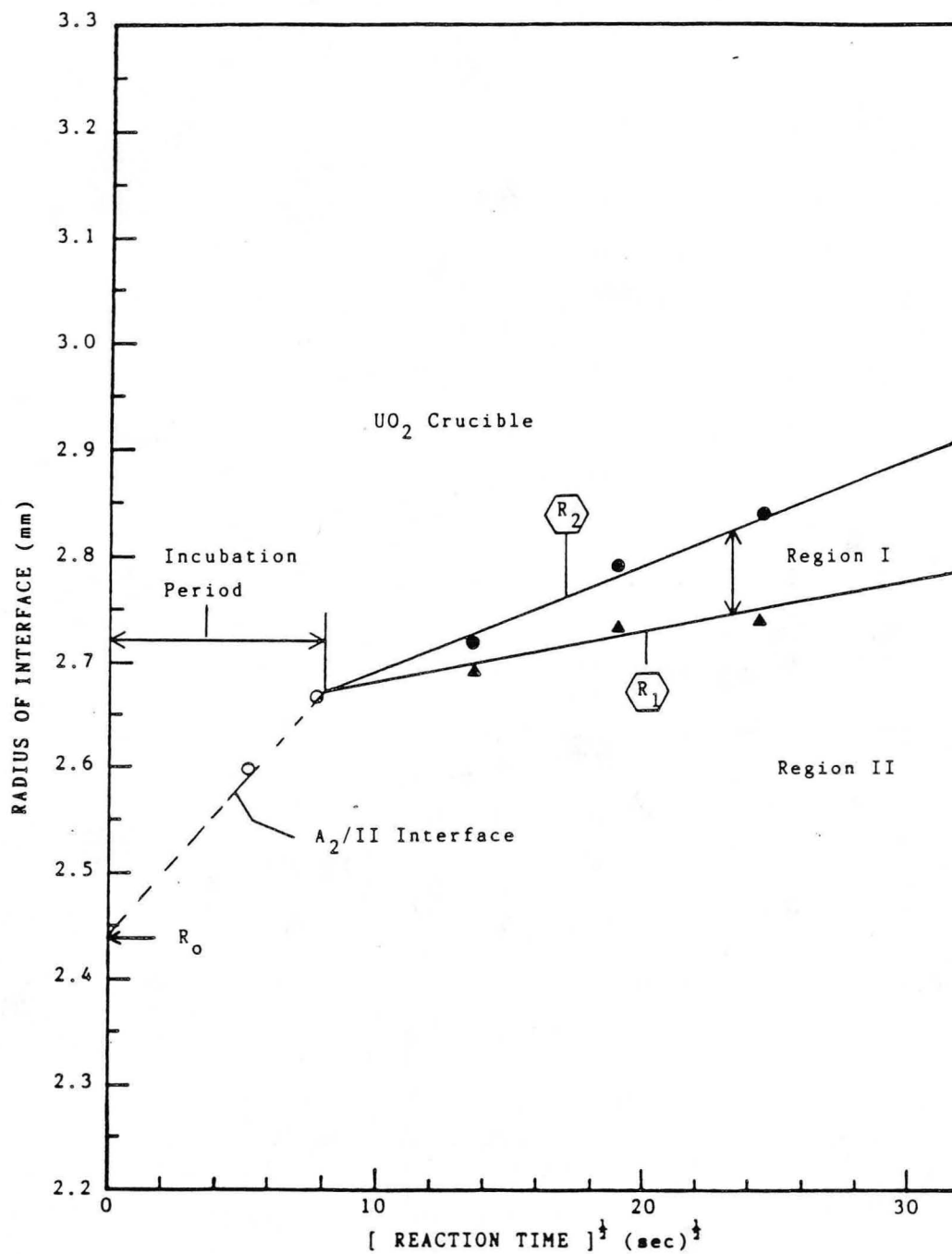


Fig. 3.38 Movement of the Reaction Layers in the UO₂ Crucible/Pure Zry System. (T=2100 °C)

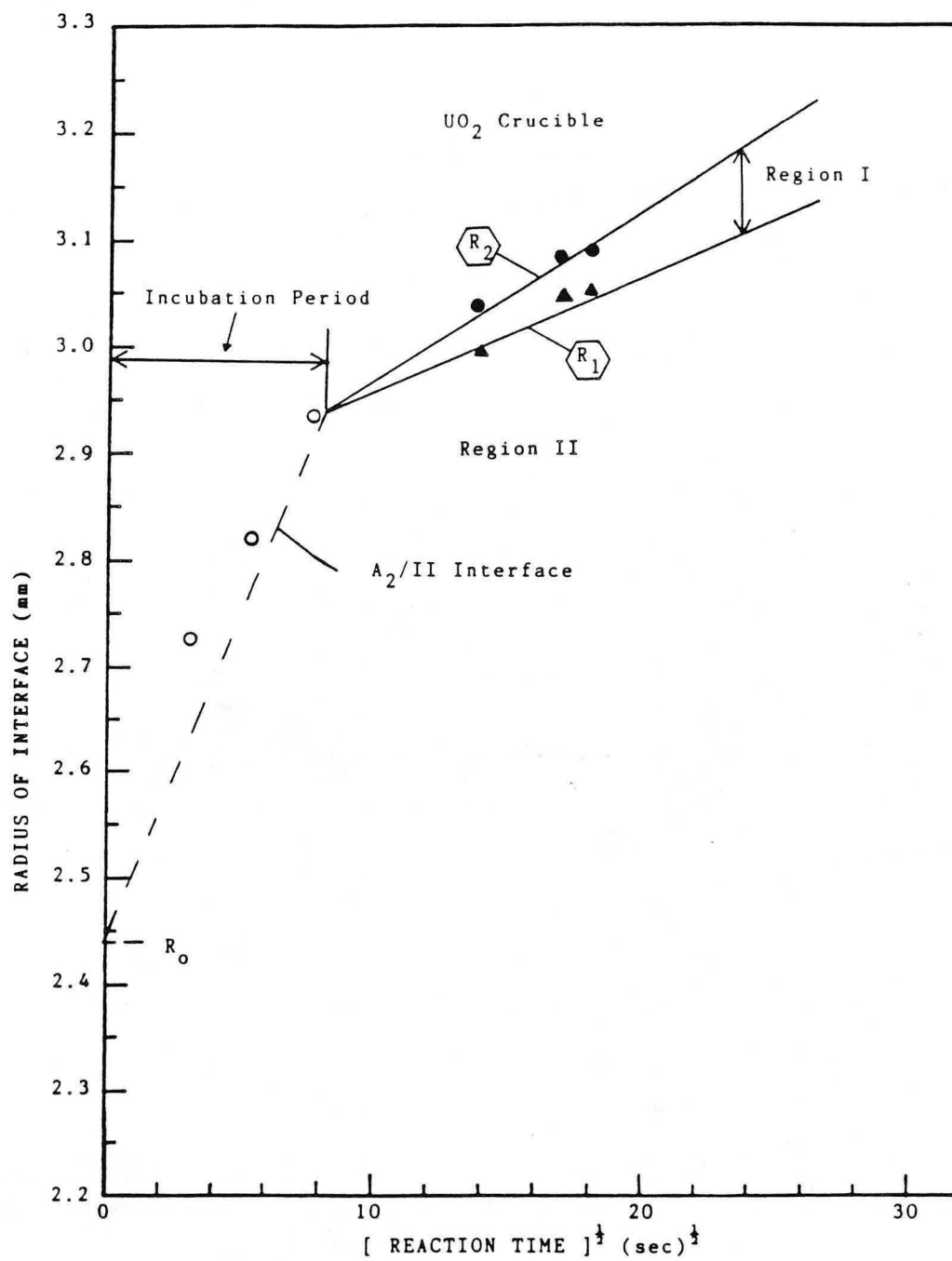


Fig. 3.39 Movement of the Reaction Layers in the UO₂ Crucible/Pure Zry System. (T=2200 °C)

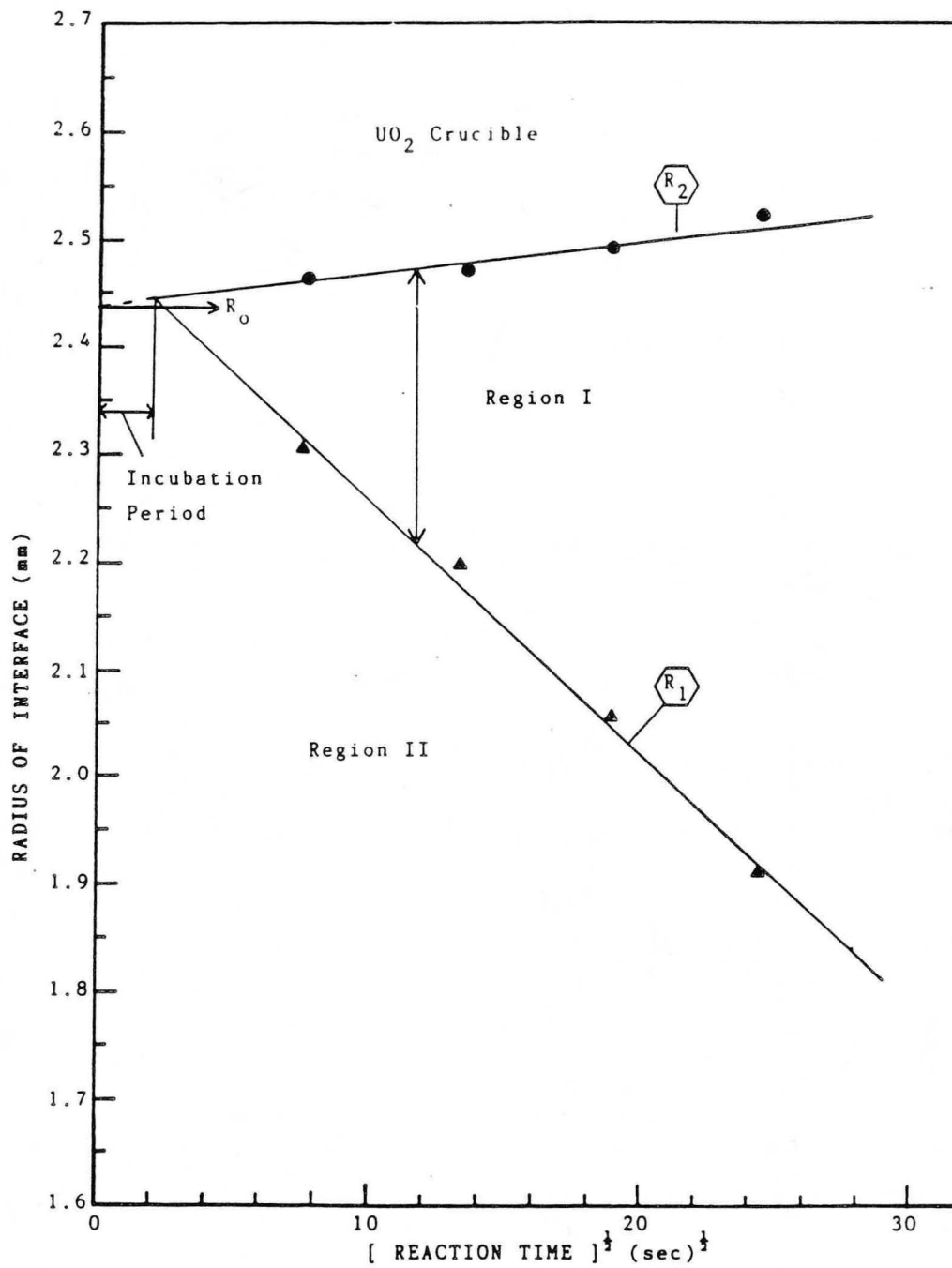


Fig. 3.40 Movement of the Reaction Layers in the UO₂ Crucible/6.0w/o O-Zry System. (T=2100 °C)

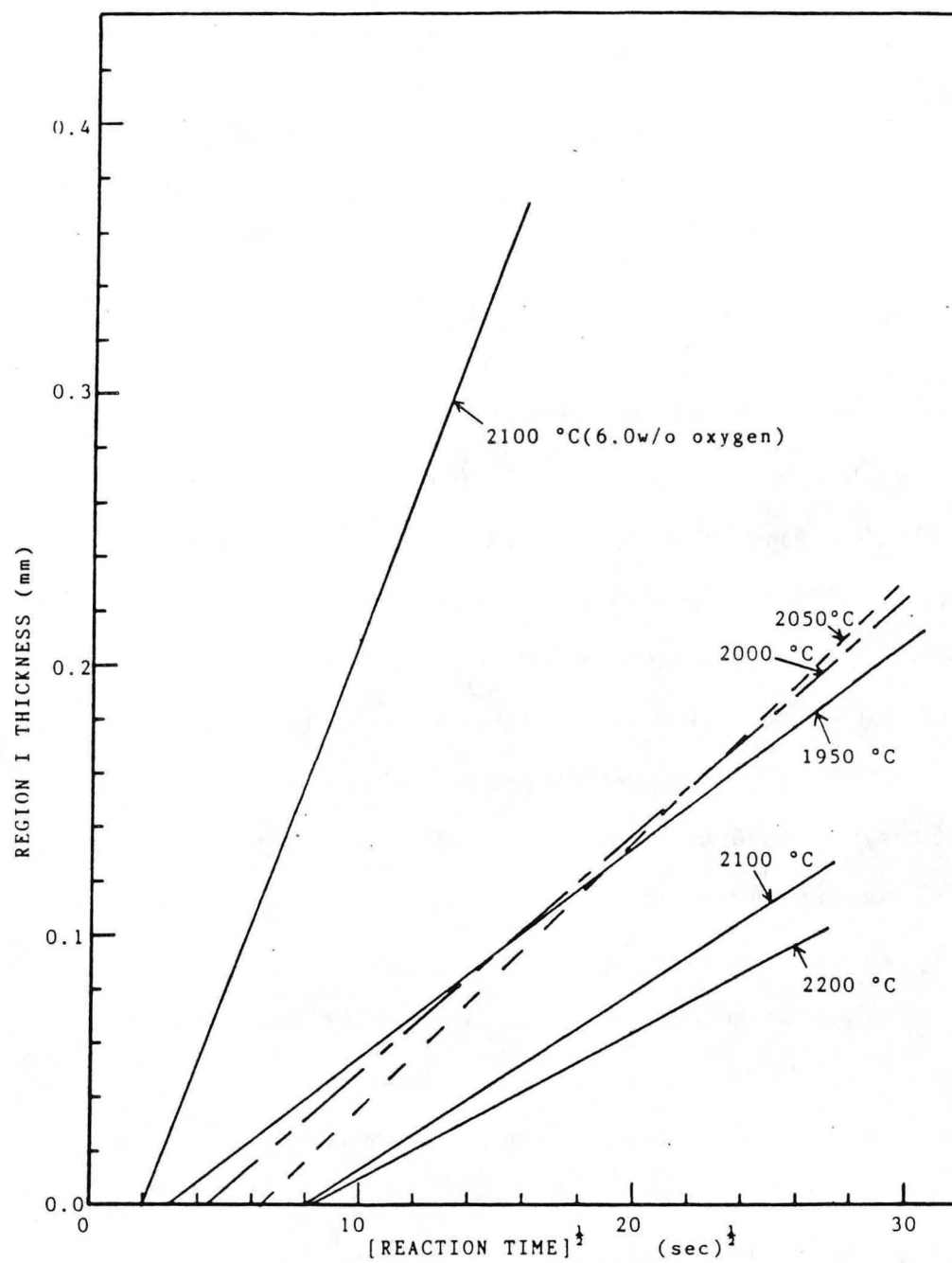


Fig.3.41 Region I Thickness versus $(\text{Reaction Time})^{1/2}$
at the Various Reaction Temperatures.

$$\begin{array}{ll}
 X^2/(t - 14.1) = 7.1 \times 10^{-7} & \text{at } 2000^\circ \text{ C} \\
 X^2/(t - 33.1) = 8.5 \times 10^{-7} & \text{at } 2050^\circ \text{ C} \\
 X^2/(t - 68.1) = 4.4 \times 10^{-7} & \text{at } 2100^\circ \text{ C} \\
 X^2/(t - 76.6) = 3.1 \times 10^{-7} & \text{at } 2200^\circ \text{ C} \\
 X^2/(t - 3.1) = 6.8 \times 10^{-6} & \text{at } 2100^\circ \text{ C (6.0w/o O-Zry)}
 \end{array}$$

where the growth rate coefficient is in cm^2/s and t is in second.

In this system, the uranium concentration in region II, which was uniform and measured by X-ray fluorescence spectrometry(XFS), was considered to be the amount of uranium dissolved. This measurement is in contrast to the UO_2 disk experiments, in which the amount of uranium dissolution was obtained by comparison of the original thickness of the UO_2 disk with its thickness after reaction(see Fig. A.1). In Fig. 3.42, the uranium concentrations(on an oxygen-free basis) in region II measured by XFS are plotted versus the square root of time for the various temperatures. This figure shows that, during the incubation period(dotted curves), the rate of uranium dissolution is quite large and depends greatly on reaction temperature, reaction time and the initial oxygen content of the Zry. This figure also suggests that, after the incubation period(solid lines), the rate of uranium dissolution is governed by the parabolic rate law. However, the data points can just as well be viewed as approaching a saturation value, as shown in Fig. 3.43. We consider that the apparent parabolic relationship following the incubation period is not real, and that the primary uranium dissolution mechanism involves processes other than simple diffusion.

The ceramic phase[(U,Zr) O_2 and (U,Zr) O_{2-x}] contents in region II were determined using an image analyzer. The ceramic phase contents shown in Fig. 3.44 are consistent with uranium concentration results in Fig. 3.42 because there is an one-to-one relationship between uranium content and ceramic phase content(9). Comparison with Hofmann's results(9) shown in Fig. 3.45, however, shows that the present data exhibit a larger content of

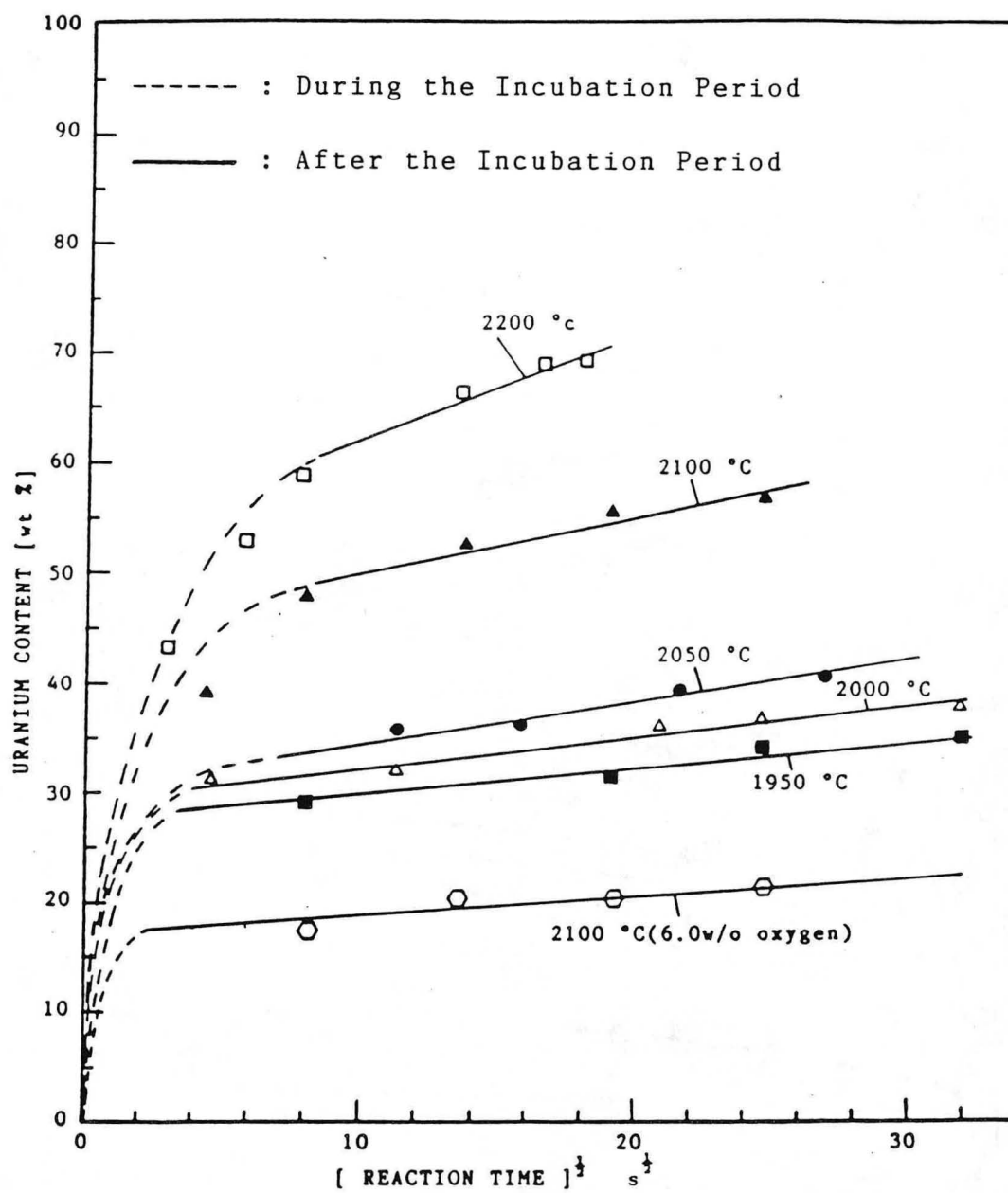


Fig.3.42 Uranium Content in Region II versus (Reaction Time)^{1/2} at Various Reaction Temperatures, Measured by XFS.

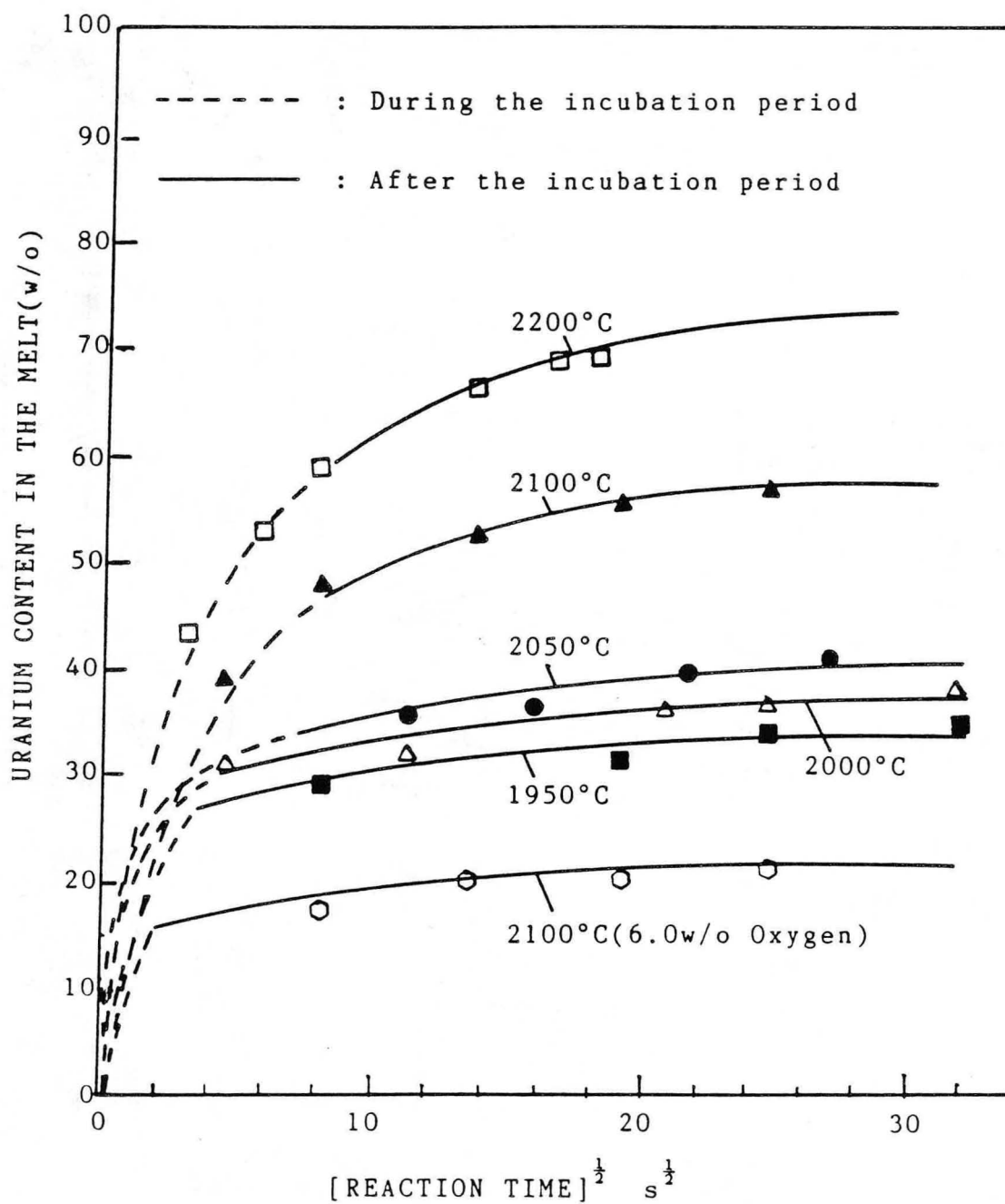


Fig. 3.43 Uranium Content in Region II versus (Reaction Time)^{1/2} at Various Reaction Temperatures, Measured by XFS.

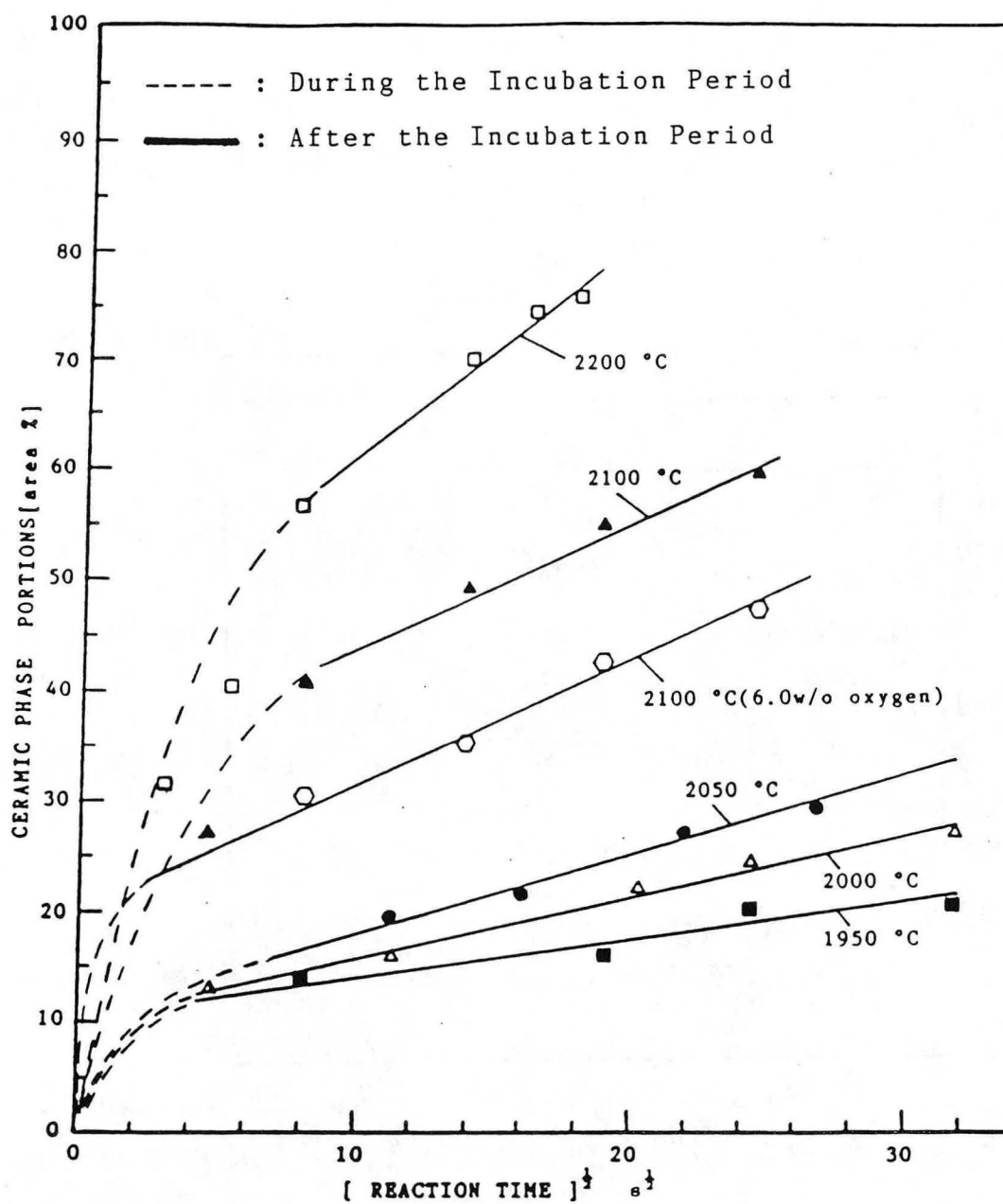


Fig.3.44 Ceramic Phase Portions in Region II versus $(\text{Reaction Time})^{1/2}$ at Various Reaction Temperatures.

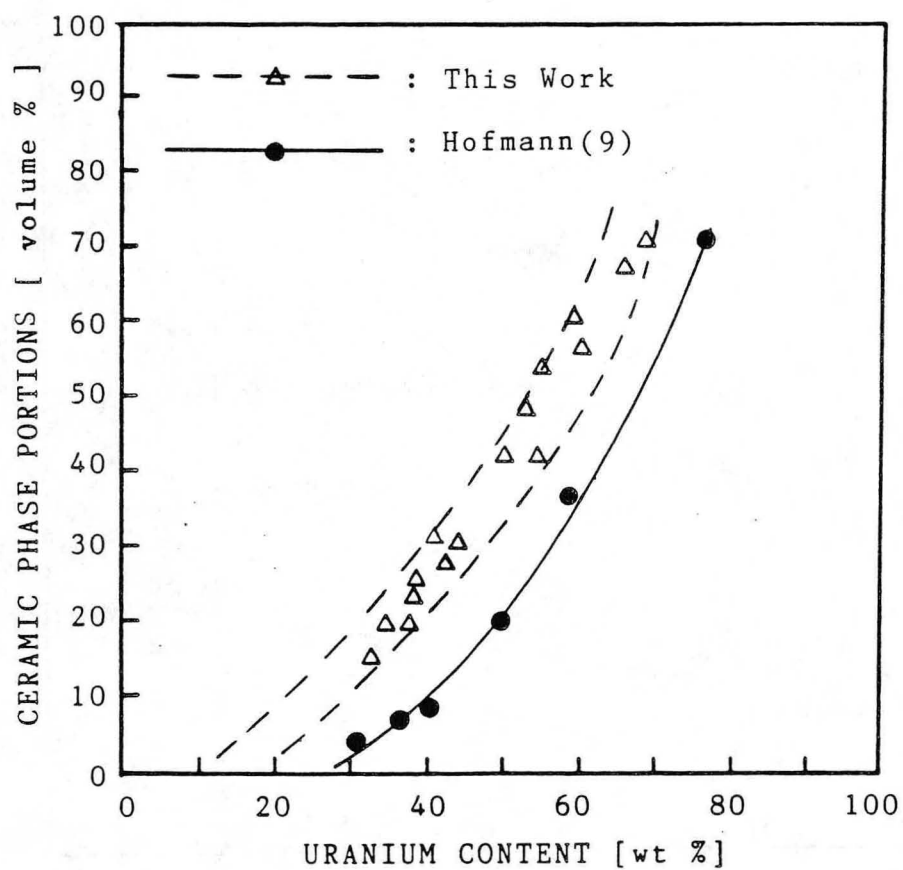


Fig.3.45 Correlation between the U Content and the Ceramic Phase Portion in Region II.

the ceramic phases for a given uranium content. This difference arises from the technique Hofmann used to obtain the data in Fig. 3.45 ; he mixed UO_2 and Zry and melted the entire mixture, thus fixing the oxygen content of the melt. In our case, on the other hand, more oxygen than uranium is extracted from the initially stoichiometric UO_2 crucible, thereby leaving the O/U ratio of the crucible less than 2 and the O/U ratio in the melt greater than 2 (see Fig. 3.33). The two experiments are thus qualitatively consistent.

The rates of increase of the uranium concentration and the ceramic phase content in region II after the incubation period are plotted versus reciprocal temperature in Fig. 3.46. In order to determine activation energies, the least square method was used. The results are :

Rate of increase of the uranium concentration after the incubation period :

$$\frac{[C_{U_{II}}(t) - C_{U_{II}}(t_0)]^2}{t - t_0} = 1.1 \times 10^{10} \exp(-116 / RT)$$

Rate of increase of the ceramic phase fraction after the incubation period :

$$\frac{[f_{cer}(t) - f_{cer}(t_0)]^2}{t - t_0} = 1.6 \times 10^{11} \exp(-122 / RT)$$

where t_0 = an incubation period (in seconds) which depends on reaction temperature, $C_{U_{II}}(t)$ = wt % uranium of region II at t and $f_{cer}(t)$ = volume percent of region II consisting of ceramic phases at t . Activation energies are in kcal/mole.

However, as noted earlier, the parabolic behavior is only apparent ; so the activation energies in the above formulas do not have any fundamental physical significance. The discrepancy between the above activation energies and that reported by Hofmann (160 kcal/mole in Ref. 9) is probably not significant, particularly since he did not explicitly remove the incubation period t_0 for estimating parabolic rate constants ; however, the discrepancy between the above activation energies and that for disk dissolution (see section 3.1.3) is also

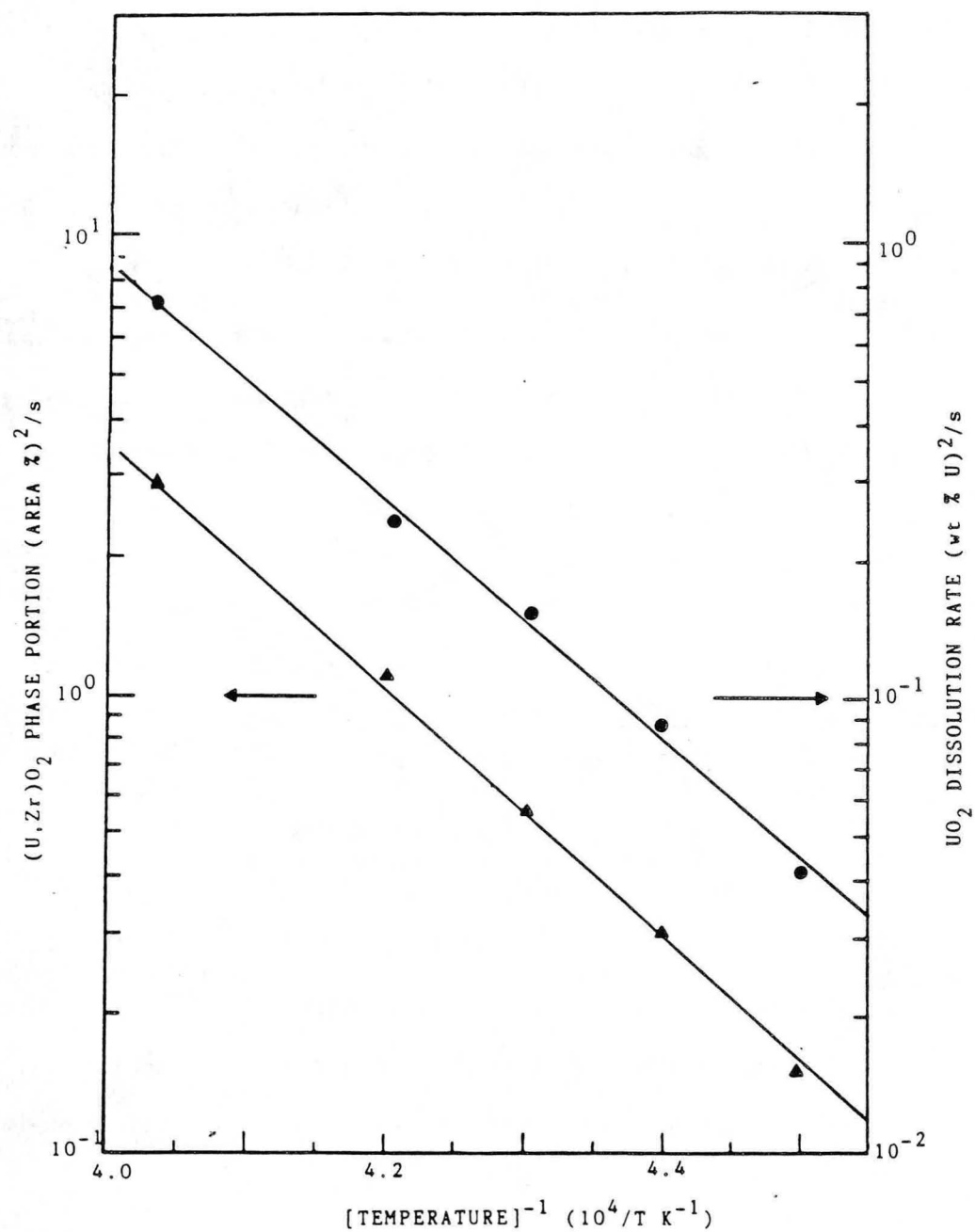


Fig. 3.46 UO₂ Dissolution Rate and Ceramic Phase Portion as a Function of Reciprocal Temperature.

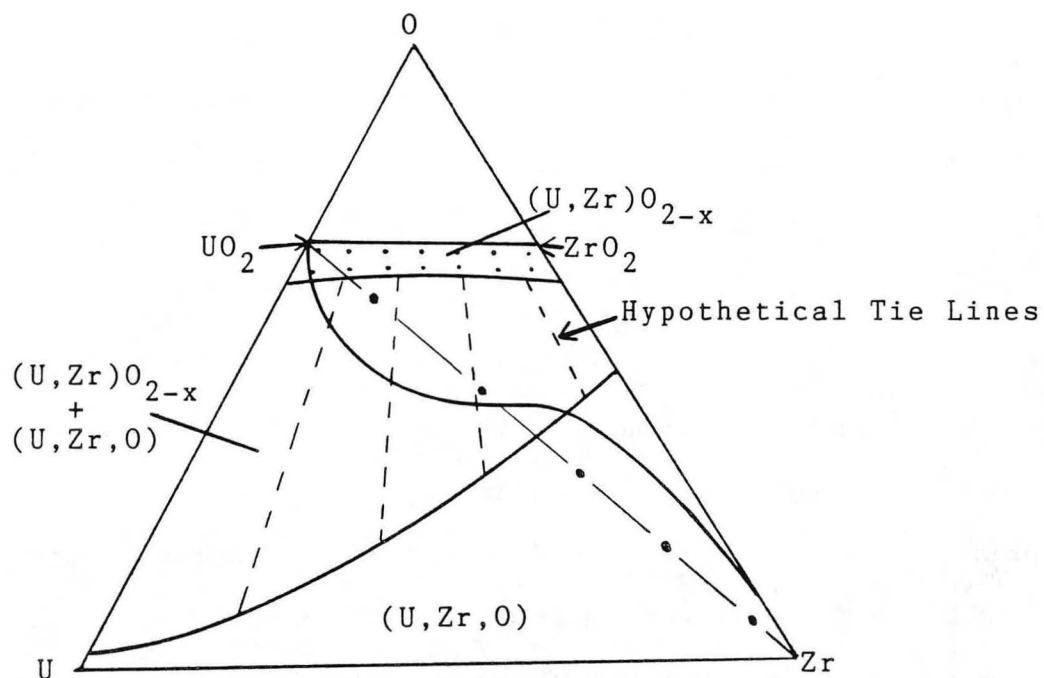
not important.

4 DISCUSSION

4.1 Phase Changes during Cooling-Down

The overall average composition variation across the specimen gives the diffusion path at the reaction temperature, under the assumption that no average composition changes occur across the specimen during cooling-down. Even though this is not strictly true because of liquid motion, the existence of a layered structure in the postannealed specimen indicates that liquid motion did not greatly perturb the average compositional distribution during cooling-down. The overall average compositional variations for the polycrystalline UO_2 disk/molten Zry system are shown in Figs. 3.13 through 3.15. Using these curves, the diffusion paths at 2000 °C for the various initial oxygen contents of the Zry were drawn in Fig. 3.16. The diffusion path of the polycrystalline UO_2 disk/pure Zry at 2000 °C (Fig. 3.16-a), however, was redrawn in Fig. 4.1. Note that the ternary phase diagram at 2000 °C contains two single phase regions, the solid mixed oxide $(\text{U,Zr})\text{O}_{2-x}$ and the (U,Zr,O) liquid, and the two-phase region between the two. The diffusion path shown in Fig. 4.1 satisfies the restrictions applied to single region and multi-phase region (28, 29, 30) and crosses the dash-dot straight line joining the terminal compositions only once, which is a simple consequence of mass balance (31). In addition, this diffusion path cuts across the tie lines in the two-phase region and goes through the (U,Zr,O) melt region. As a result, this diffusion path produces the reaction layers and products at 2000 °C, as shown in Fig. 4.1. The phases which exist at room temperature (Fig. 3.1), therefore, resulted from transformation and decomposition of the simple reaction-temperature phases during cooling-down.

In order to predict the transformed or decomposed phases, the C-T (continuous cooling curve versus temperature) diagram of the U-Zr-O system and cooling rates must be known. In practice, the three-dimensional U-Zr-O phase diagram is not complete and the C-T diagrams cannot be determined. A qualitative assessment of phase changes during cooling-down, however, can be made by two approximate methods : a) equilibrium phase changes



a) Reaction Layers and Products at 2000°C

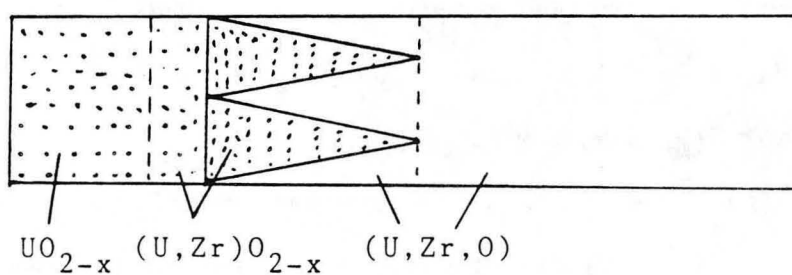
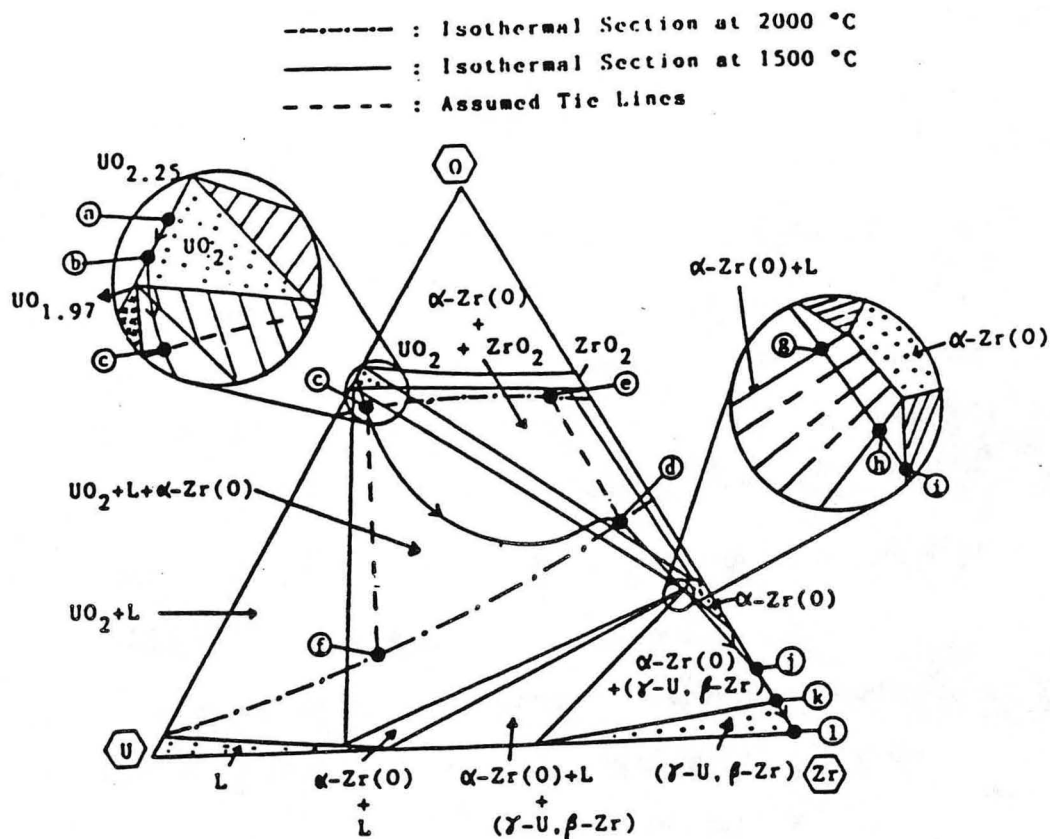


Fig.4.1 Reaction Layers and Products at 2000°C Produced by the Diffusion Path for the Polycrystalline UO_2 Disk/Pure Zry System.

accompanying infinitesimal temperature variations and b) quenching to the freezing temperature. The former is applicable to slow cooling. The latter, in which it is assumed that no phase changes occur until the freezing temperature is reached, is applicable to rapid cooling. Fig. 2.3, however, indicates that the specimens tested in the present work cooled down rapidly. The latter, therefore, is more applicable to the present experiment.

For the polycrystalline UO_2 disk/pure Zry system, the layer sequence observed in the postannealed specimen was predicted by combining the diffusion path (Fig. 4.1) with the method of quenching to the freezing temperature. Here, the freezing temperature of the specimens tested in the present work was assumed to be 1500°C , because there is only one liquid phase in the ternary isothermal section at this temperature (Fig. 1.1). The reaction layers and products predicted at 1500°C are shown in Fig. 4.2. This figure shows that the a-b segment of the diffusion path produces UO_{2-x} . The b-c segment, which represents $(\text{U,Zr})\text{O}_{2-x}$ at 2000°C , produces $[\text{UO}_2 + \text{ZrO}_2 + \alpha\text{-Zr(O)} + \text{L}]$. The c-d segment represents the average compositional variation across the two-phase region at 2000°C . This region gives the coexisting true compositional segments, c-e (for the solid part of the two-phase region) and f-d (for the liquid part), based on the hypothetical tie lines. The quenched solid phase from the solid part of the two-phase region at 2000°C produces $[\text{UO}_2 + \text{ZrO}_2 + \alpha\text{-Zr(O)} + \text{L}]$ (towards "e") and the liquid part produces $[\text{UO}_2 + \alpha\text{-Zr(O)} + \text{L}]$. The d-g segment, which represents the (U,Zr,O) melt at 2000°C , produces various combinations of $[\text{UO}_2 + \text{ZrO}_2 + \alpha\text{-Zr(O)} + \text{L}]$, depending on the exact location on the d-g segment. Finally, the g-h segment produces $[\alpha\text{-Zr(O)} + \text{L}]$, the h-i segment $[\alpha\text{-Zr(O)} + \text{L} + (\gamma\text{-U}, \beta\text{-Zr})]$, the i-j segment $[\alpha\text{-Zr(O)} + (\gamma\text{-U}, \beta\text{-Zr})]$, the j-k segment $[\alpha\text{-Zr(O)} + \text{prior } \beta\text{-Zry}]$, and the k-l segment prior $\beta\text{-Zry}$.

From Fig. 4.2, it is seen that some of layers have more than two phases. This is not an exception to the rule that layers with more than two phases never form during isothermal diffusion in a ternary system. Comparison of the predicted phases with the phases observed at room temperature (Fig. 4.2) shows that UO_{2-x} at 1500°C (path a-b) decomposes to $[\text{UO}_2 +$



REGIONS	A ₁	A ₂	I		II _a		II _b	III	IV
PREDICTED LAYERS at 1500 °C	UO _{2-x}	UO ₂ +ZrO ₂ + α-Zr(O)+L	UO ₂ +ZrO ₂ + α-Zr(O)+L	UO ₂ +ZrO ₂ + α-Zr(O)+L	α-Zr(O) + L	α-Zr(O)+L + (γ-U, β-Zr)	α-Zr(O) + (γ-U, β-Zr)	α-Zr(O) + prior β-Zry	prior β-Zry
DIFFUSION PATH	a - b	b - c	c - d	d - e	e - f	f - g	g - h	h - i	i - j
OBSERVED LAYERS at ROOM TEMP.	UO ₂ + U	(U,Zr)O _{2-x}	(U,Zr)O _{2-x} + α-Zr(O) + (U,Zr) _a *		α-Zr(O) + (U,Zr) _a *		α-Zr(O) + (U,Zr) _b *	α-Zr(O) + prior β-Zry	prior β-Zry

* (U,Zr)_a represents L and (U,Zr)_b represents (γ-U, β-Zr) in the U-Zr-O isothermal section at 1500 °C.

Fig.4.2 Reaction Layers and Products Predicted at 1500 °C
Based on the Diffusion Path of Polycrystalline UO₂
Disk/pure Zry System.

U] during cooling-down to room temperature. In addition, $(\text{U,Zr})\text{O}_{2-x}$ at 2000 °C(paths b-c and c-e) does not decompose to $[\text{UO}_2 + \text{ZrO}_2]$ or $[\text{UO}_2 + \text{ZrO}_2 + \alpha\text{-Zr(O)}]$. On the other hand, it was very difficult to identify the predicted three-phase region, $[\alpha\text{-Zr(O)} + \text{L} + (\gamma\text{-U}, \beta\text{-Zr})]$. This hidden three-phase region, however, was included in the $[\alpha\text{-Zr(O)} + \text{L}]$ region for the purpose of identifying the reaction layers. Therefore, the layer sequence and reaction products predicted by the method of quenching to the freezing temperature agree well with those observed at room temperature.

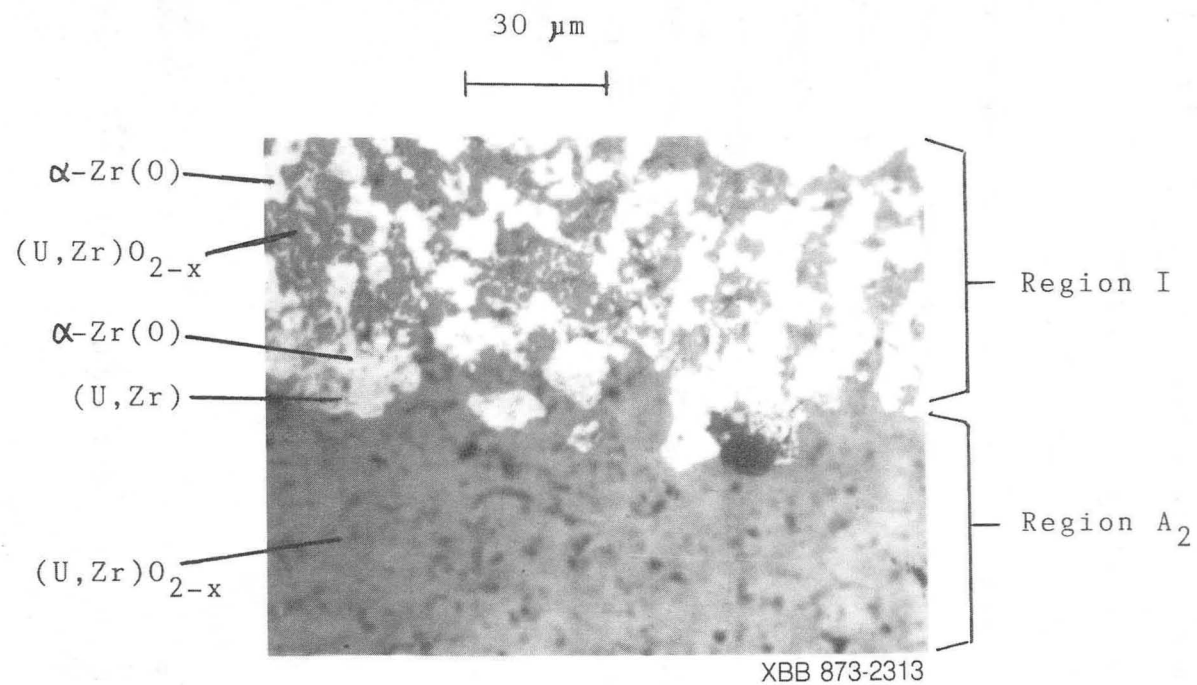
Similar explanations for the 2.4w/o O-Zry and 5.0w/o O-Zry systems can be given.

The predicted transformed phases obtained from the lower-temperature phase diagrams during cooling-down give no information about the final microstructure. The microstructure differs widely from system to system(i.e., eutectic or peritectic), depending on the relative portion of the existing phases and on the cooling rates.

4.2 Dissolution Mechanism and Reaction Kinetics

4.2.1 UO_2 Single Crystal / Molten Zry System

The interface between UO_2 and molten Zry(Fig. 4.3) shows evidence of the preferential attack of the molten Zry into some parts of the UO_2 bulk region to form disintegrating $(\text{U,Zr})\text{O}_{2-x}$ particles(gray phase) through region I and to form a porous-medium-like structure of partially dissolved $(\text{U,Zr})\text{O}_{2-x}$ at the A_2/I interface. This behavior is difficult to rationalize because there are no grain boundaries in a single crystal. Some preferential pathway for penetration of the molten Zry, therefore, must have been created in order to exhibit the type of attack seen in Fig. 4.3. This figure shows that the porous-medium-like structure at the A_2/I interface contains particles which are Zr(O) on the top and (U,Zr) on the bottom. These particles are liquid phase at the reaction temperature and connected to the bulk (U,Zr,O) melt in region I, even though they appear isolated from the bulk melt in this figure. This phenomenon indicates that the preferential loss of oxygen possibly along the subgrain boundaries or dislocations causes small portions of liquid uranium to form along the subgrain

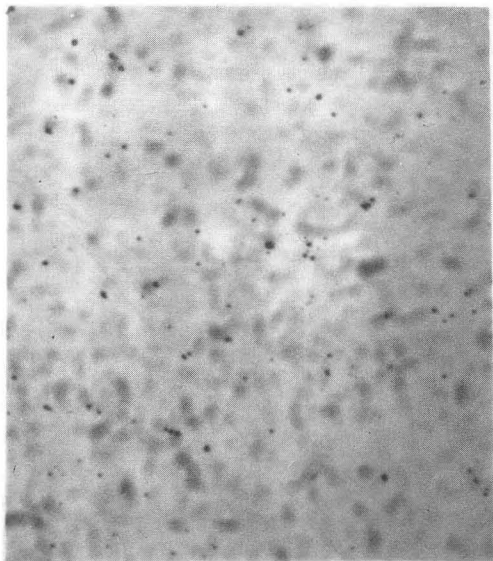


As-polished Specimen

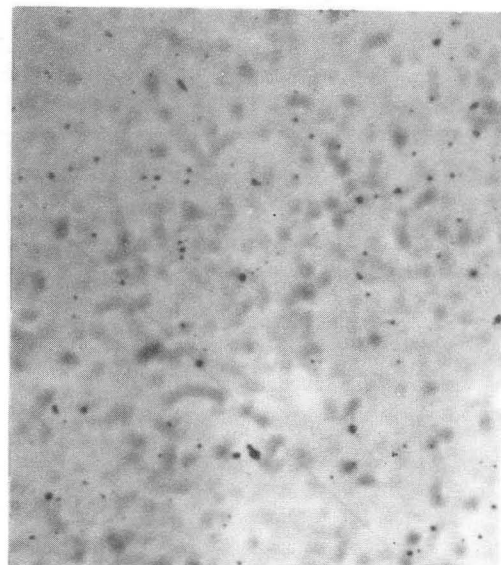
Fig. 4.3 UO_2 Single Crystal/Molten Zry Interface Appearance(Optical).
($T=2000^\circ\text{C}$, $t=60\text{ s}$)

boundaries or dislocations in direct contact with the molten Zry. Subsequent penetration of the molten Zry along this liquid uranium interlayer accelerates the formation of liquid uranium within the UO_{2-x} bulk region, thus producing the porous-medium-like structure at the A_2/I interface and eventually causing separation of tiny $(\text{U,Zr})\text{O}_{2-x}$ particles in region I.

Fig. 3.18 shows that UO_2 has two distinct regions, $[(\text{U,Zr})\text{O}_{2-x}](A_2)$ and $[\text{UO}_2 + \text{U}](A_1)$. In region A_2 , there are very few pores and metal particles, probably because zirconium stabilizes UO_{2-x} even at room temperature. In region A_1 , uniformly-distributed pores and metal particles were observed, which indicates that the oxygen diffusivity is much faster in the UO_2 than in the molten Zry, and most of metal particles are associated with pores. Comparison of the as-received UO_2 with the specimen heated without Zry (Fig. 4.4) shows that there is no apparent microstructural difference between them. Comparison of the UO_2 heated with and without Zry (Fig. 3.18 and 4.4), however, clearly shows that the former has much higher porosity. The uniformly-distributed pores, therefore, must have been created during cooling-down by the decomposition of UO_{2-x} to $[\text{UO}_2 + \text{U}]$. The decomposition would cause extra void volume in the $[\text{UO}_2 + \text{U}]$ region due to the approximately factor-of-two higher density of uranium compared with that of UO_{2-x} . Consequently, the uranium precipitates formed by the decomposition of UO_{2-x} should be associated with pores, which is consistent with the observed phenomenon (see Fig. 3.18). In addition, the created porosity should be the same as volume percent of the uranium precipitates. In order to confirm this pore-creation mechanism, quantitative data on porosity and volume fraction of uranium precipitate were determined by using an image analyzer. The results are shown in Fig. 4.5. This figure shows that porosity and metal particles are uniformly distributed except in region A_2 . The expected porosity is defined as the as-received porosity plus the created porosity. The created porosity is assumed to be the same as the volume fraction of the uranium precipitate, because the density of uranium metal is approximately twice that of UO_2 . Comparison of the observed porosity with the expected porosity (Fig. 4.6) shows good agreement, which confirms the pore-creation mechanism.



As-received UO_2



XBB 873-2311

Heated UO_2
($T=2000^\circ\text{C}$, 90 s)

Fig. 4.4 Microstructural Difference between the As-received and the without Zry Heated UO_2 Single Crystal. (Optical)

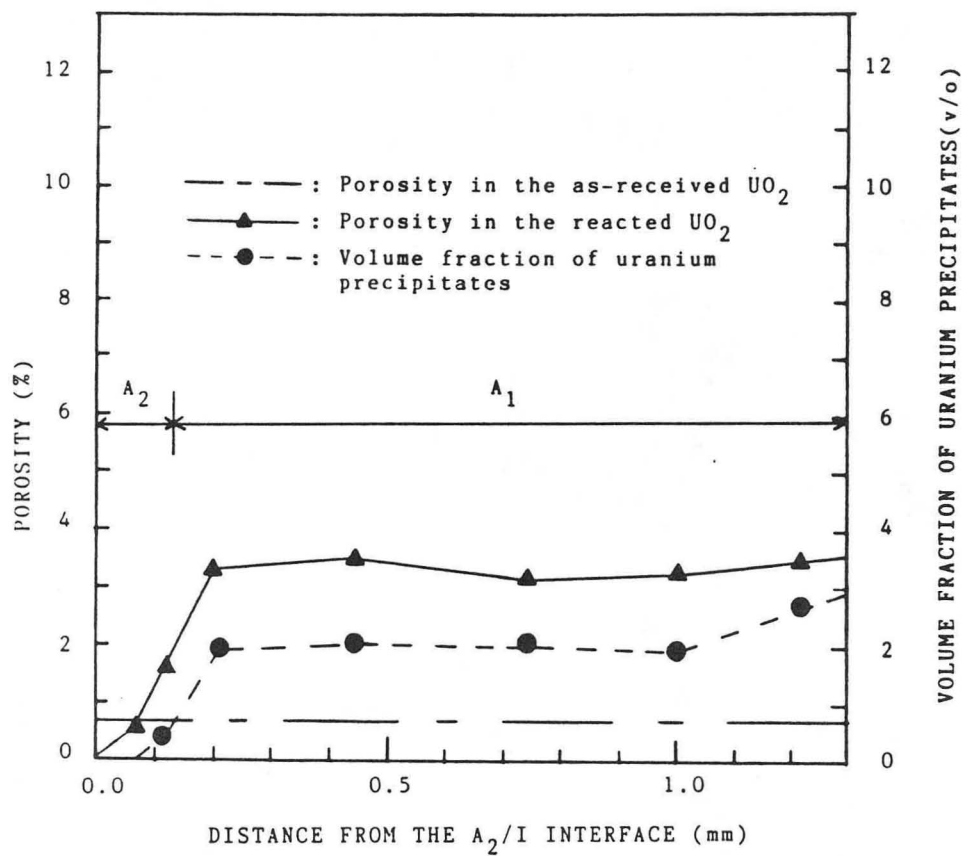


Fig.4.5 Porosity and Volume Fraction of Uranium Precipitates in Regions A_1 and A_2 for the UO_2 Single Crystal/Molten Zry System.
[$T=2000^\circ\text{C}$ & $t=60\text{s}$]

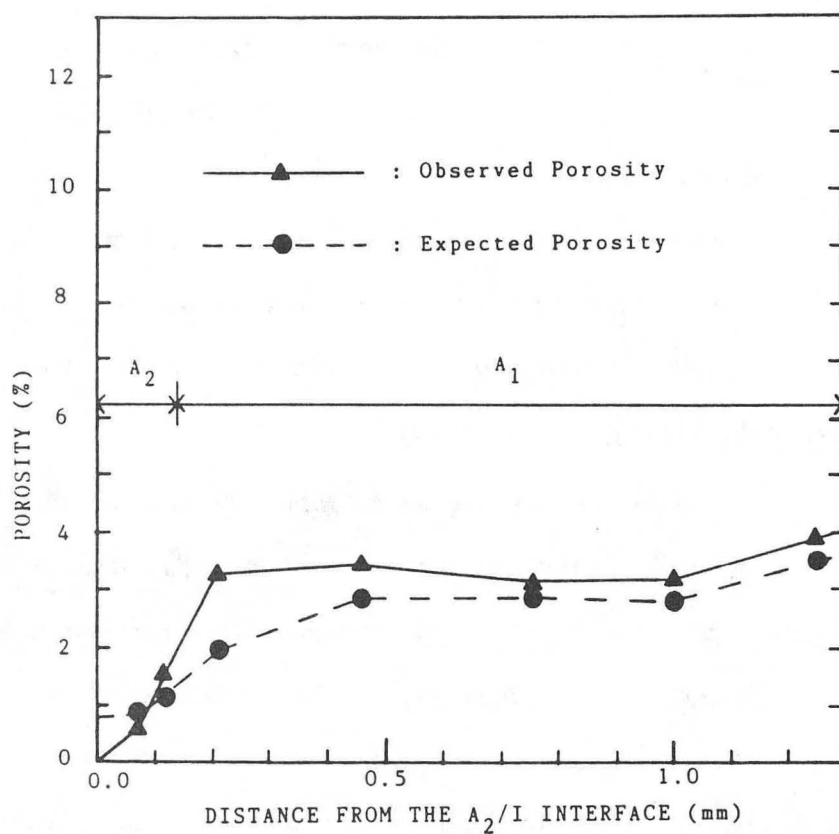


Fig. 4.6 Comparison of the Observed Porosity with the Expected Porosity for the UO_2 Single Crystal/Molten Zry System. ($T=2000\text{ }^{\circ}\text{C}$, $t=60\text{s}$)

Based on the microstructures of regions A_1 , A_2 and I, the dissolution mechanism of UO_2 single crystal is sketched in Fig. 4.7. This figure shows that the molten Zry reduces UO_2 to UO_{2-x} with no detectable oxygen gradient through the UO_2 single crystal sphere since zirconium is a more powerful reducing agent than uranium. Molten Zry further reduces UO_{2-x} to $UO_{2-x'}$ plus liquid uranium possibly along the subgrain boundaries or dislocations in the UO_{2-x} in direct contact with the molten Zry. The molten Zry penetrates through this liquid uranium interlayer to form the (U,Zr,O) channel and Zr^{4+} diffuses into the UO_{2-x} grains to form the (U,Zr) O_{2-x} solid solutions. In addition, ingress of zirconium enlarges this liquid interlayer thickness, thus enhancing oxygen transport to the melt along this interlayer. Consequently, the porous-medium-like structure and the separate particles of (U,Zr) O_{2-x} appear in the microstructure. The separate particles become smaller and are eventually dissolved in the oxygen-poor Zry melt.

The features of the near-interface regions following interaction of UO_2 single crystals with molten Zry described by Hofmann(52) are nearly the same as those for this work. However, Hofmann argued that liquid uranium precipitates form randomly in the oxide near the UO_2 /molten Zry interface. A high-oxygen-diffusivity pathway is not invoked in this explanation. For precipitation of U(liquid) to occur within the bulk crystal at reaction temperature would require subsaturation of the oxide to promote homogeneous nucleation. Subsequently, randomly-distributed liquid uranium links up, thus causing the porous-medium-like structure and the separate particles of (U,Zr) O_{2-x} . However, it is more likely that liquid uranium forms preferentially at the UO_{2-x} in direct contact with the melt than within the bulk UO_{2-x} . In addition, the close correspondence between the volume fraction of uranium precipitates and porosity suggests that metallic uranium was not formed in region A_1 at reaction temperature.

4.2.2 Polycrystalline UO_2 Disk/Molten Zry system

A) Dissolution Mechanism

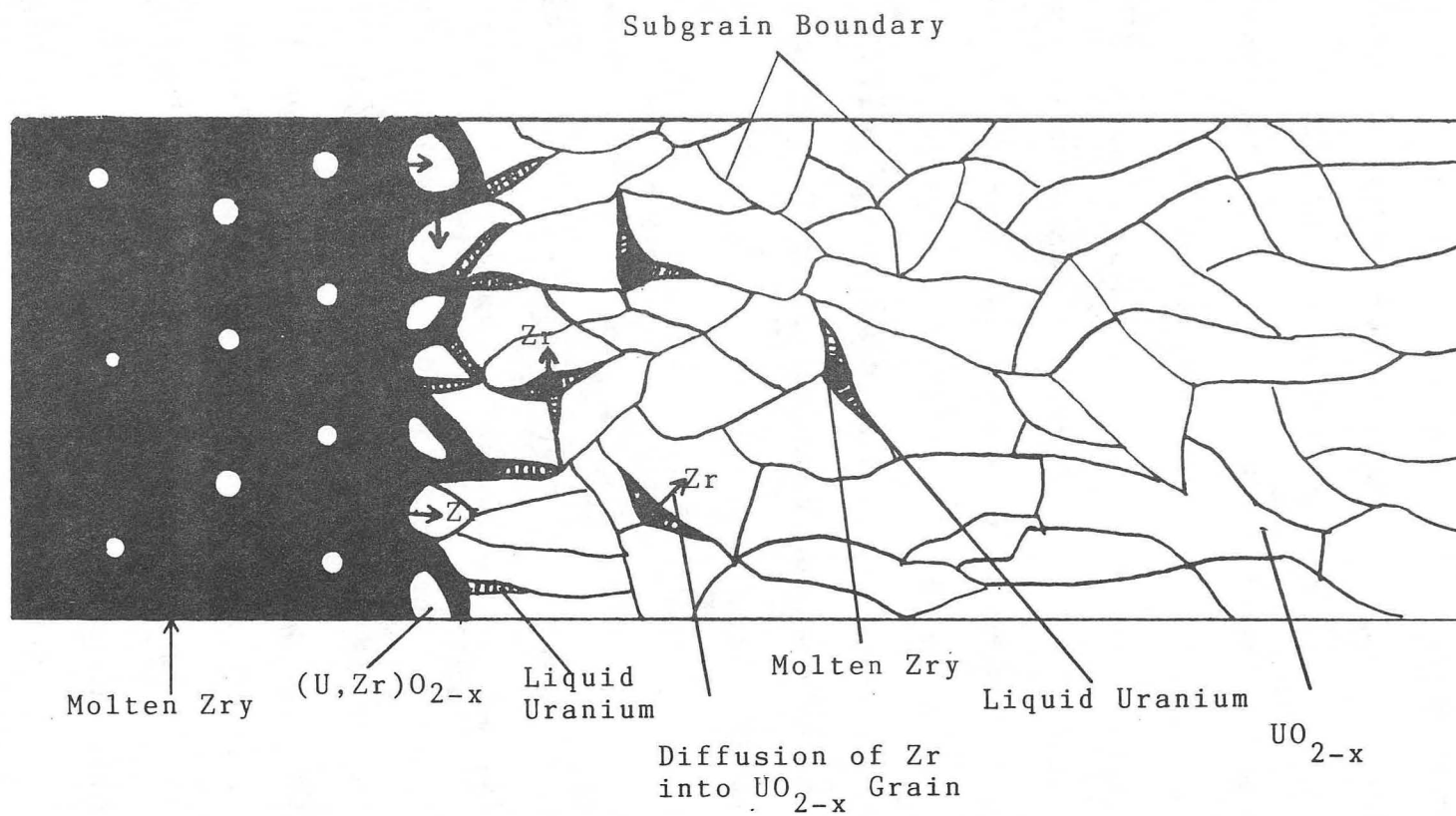
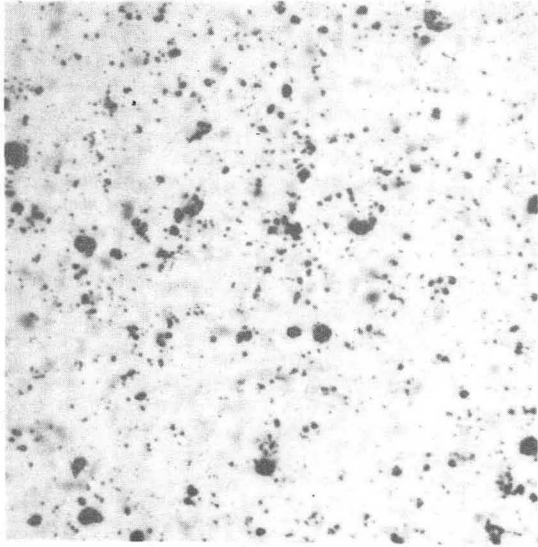


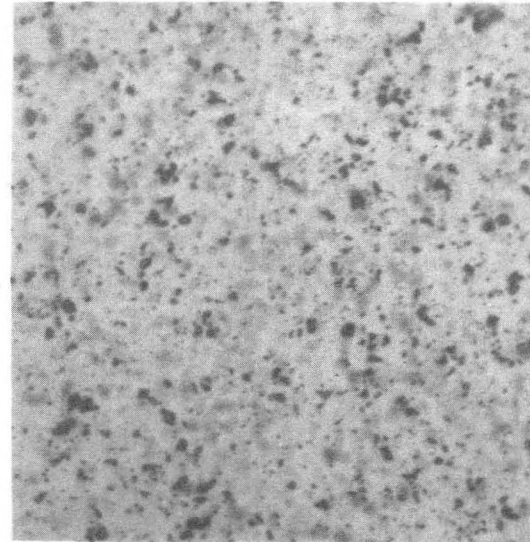
Fig.4.7 A Schematic Diagram of the Dissolution Mechanism of UO_2 Single Crystals.

Fig. 3.5 shows that the porous-medium-like structure is present near the A_2/I interface, the channel structure is formed in the middle of region I, and the separate $(U,Zr)O_{2-x}$ particles occur near the I/II interface. This microstructural change in region I indicates that the fraction of the UO_2 penetrated by the molten Zry decreases on moving towards the A_2/I interface. Note that the circular shapes of α -Zr(O) particles near region A_2 are connected to the bulk (U,Zr,O) melt in region I, even though they appear isolated from the bulk melt in this figure. Figs. 3.6, 3.9 and 3.11 show the dependence of microstructure of region I on reaction temperature and the initial oxygen content of the Zry. These figures show that the (U,Zr) channels decrease rapidly as the initial oxygen content increases and finally disappear at the 5.0w/o O-Zry system. This phenomenon occurs because the fraction of (U,Zr) channels precipitated from the (U,Zr,O) melt becomes smaller as oxygen content in the (U,Zr,O) melt increases. These figures also show that as reaction temperature or the initial oxygen content of the Zry increases, the porous-medium-like and the channel structures become much more apparent. Especially, in the case of the 5.0w/o O-Zry system(see Fig. 3.11), the porous-medium-like structure is mixed with the channel structure. The grain size of the as-fabricated UO_2 is about $10\ \mu m$, and it was found that the $(U,Zr)O_{2-x}$ particles in the channel structure possess the same size, regardless of the initial oxygen content of the Zry. On the other hand, for the pure Zry system(see Fig. 3.6), the size of the $(U,Zr)O_{2-x}$ grains(surrounded by circular shapes of α -Zr(O) particles) in the porous-medium-like structure is approximately $10\ \mu m$. For the 5.0w/o O-Zry system, however, it is much smaller than $10\ \mu m$. It is, therefore, believed that, for a relatively low oxygen content of the Zry, the molten Zry penetrates along the grain boundaries of UO_2 . In addition, for a relatively high oxygen content of the Zry, penetration of the molten Zry along the grain boundaries competes with that along the subgrain boundaries. Note that the latter is a dominant dissolution mechanism for the UO_2 single crystal/molten Zry system, as explained in section 4.2.1.

Structural differences between the as-received UO_2 and the specimen heated without Zry are shown in Fig. 4.8. This figure shows that there are no apparent structural changes.



As-received UO_2



XBB 873-2300

Heated UO_2
($T=2100^\circ\text{C}$, $t=90\text{s}$)

Fig. 4.8 Microstructural Difference between the As-received Polycrystalline UO_2 and the Specimen Heated to 2100°C for 90 s without Zry.(Optical)

The UO_2 heated with Zry(see Fig. 3.2), however, exhibits the two distinct regions A_1 and A_2 , which is consistent with the results of the UO_2 single crystal/molten Zry system(see Fig. 3.18). Region A_2 has smaller porosity and fewer metal particles than region A_1 . The detailed examination of region A_2 (Fig. 3.3) shows that some of the pores in region A_2 are filled with $\alpha\text{-Zr(O)}$. In addition, air-oxidized specimen(see Fig. 3.2) indicates that some of the metal particles in region A_1 are $\alpha\text{-Zr(O)}$ which are always found in pores. These $\alpha\text{-Zr(O)}$ particles are found even near bottom of the UO_2 disk. Calculation(Appendix B) shows that the diffusion of Zr^{+4} in the UO_2 cannot explain the observed phenomena. It is, therefore, likely that the preferential loss of oxygen along the grain boundaries may change completely the microstructure of the UO_2 (e.g., formation of open pores) : the molten Zry then penetrates preferentially along the grain boundaries with open pores. On the other hand, both the formation of liquid uranium at the reaction temperature and the decomposition of UO_{2-x} to $[\text{UO}_2 + \text{U}]$ during cooling-down will increase the size of the original pore and will also create pores. Fig. 4.9 shows the porosity and volume fraction of metal particles for various reaction temperatures, which were measured by an image analyzer. This figure shows that, as reaction temperature increases, the porosity and volume fraction of the metal particles in region A_1 increase. This figure also confirms that the porosity and volume fraction roughly uniform. These phenomena indicate that the amount of oxygen loss from the UO_2 disk is proportional to reaction time and temperature, and that the oxygen diffusivity is much faster in the UO_2 than that in the molten Zry. The expected porosity which were defined in section 4.2.1 is compared with the observed porosity in Figs. 4.10 through 4.12. These figures show that the observed porosity is nearly the same as the expected porosity, which is consistent with the results of the UO_2 single crystal/molten Zry system(see Fig. 4.7).

Based on the microstructures of regions A_1 , A_2 and I, the dissolution mechanism of polycrystalline UO_2 is sketched in Fig. 4.13. This figure shows that, at a relatively low initial oxygen content of the Zry, the molten Zry reduces UO_2 to UO_{2-x} with no oxygen gradient through the UO_2 disk. As a result of the preferential oxygen loss along the grain

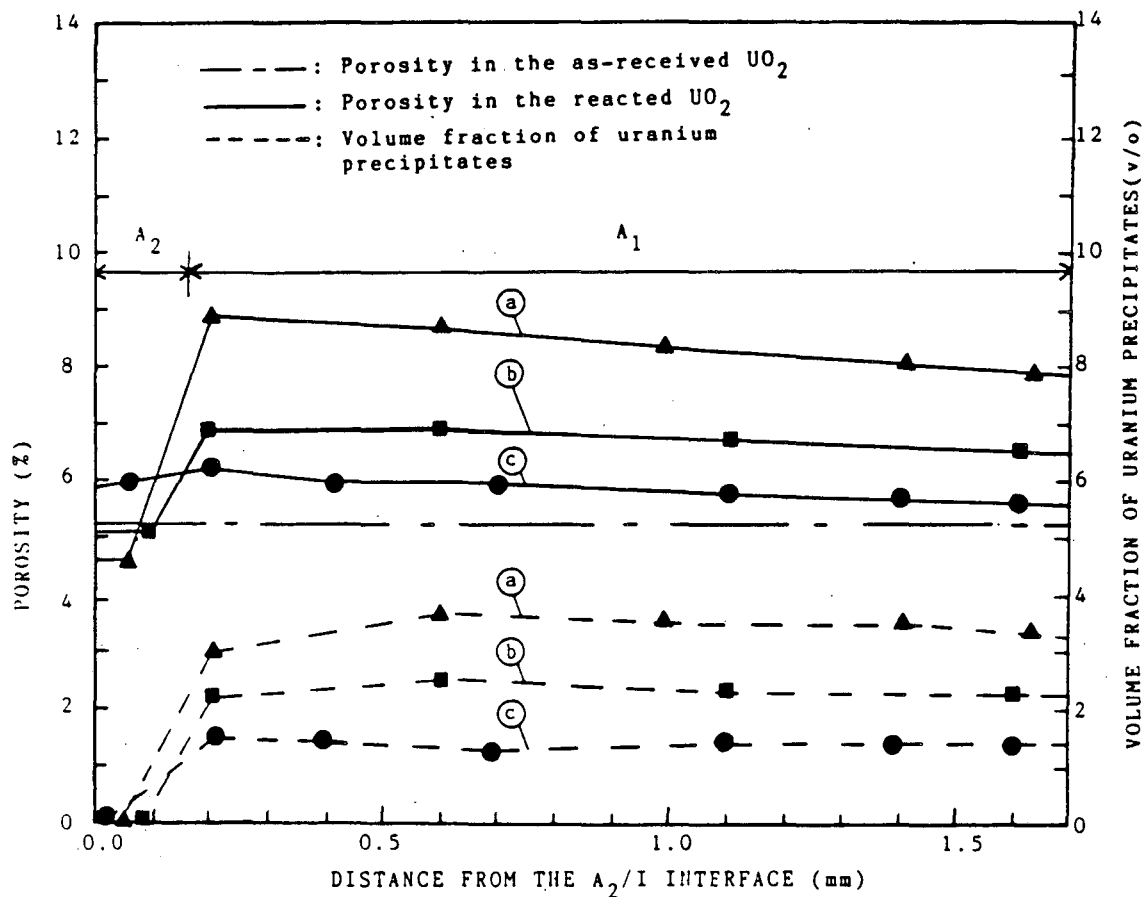


Fig.4.9 Porosity and Volume Fraction of Uranium Precipitates in Regions A_1 and A_2 for the Polycrystalline UO_2 Disk/Molten Zry System.
 [a - $T=2100^\circ C$ & $t=120s$, b - $T=2000^\circ C$ & $t=205s$,
 c - $T=1900^\circ C$ & $t=120s$]

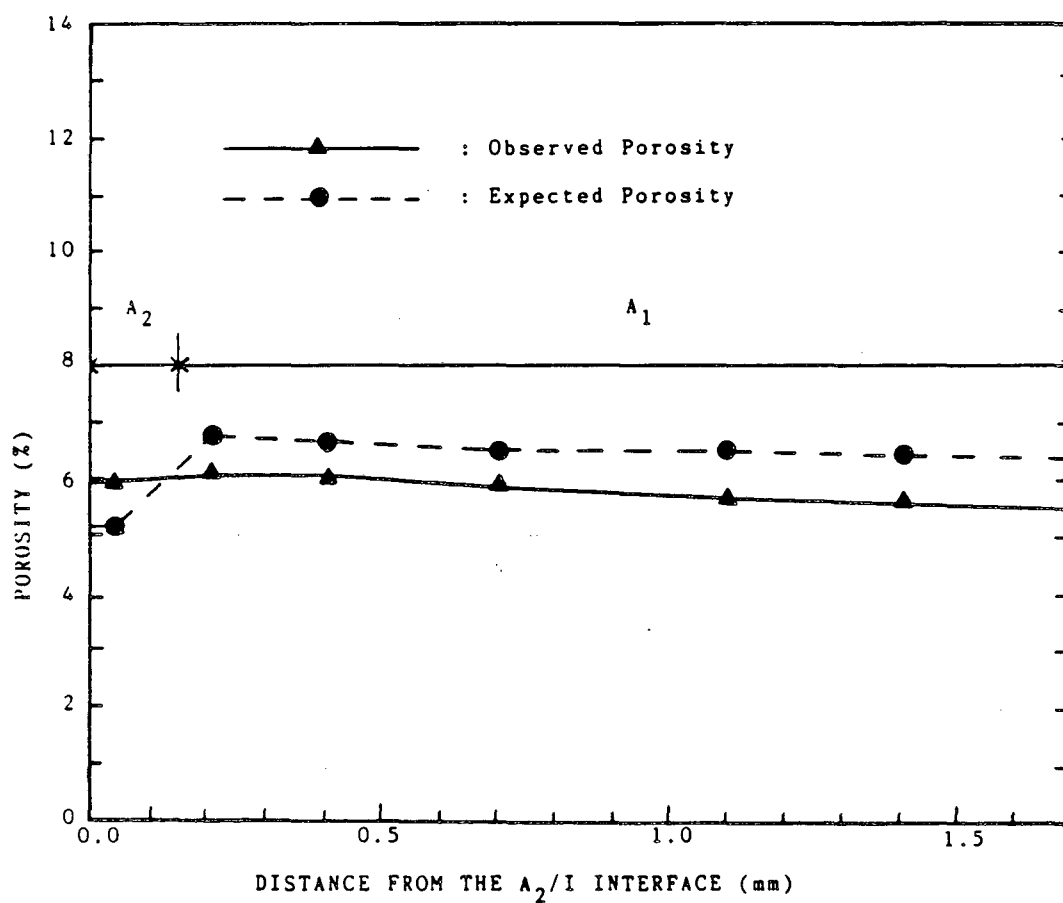


Fig. 4.10 Comparison of the Observed Porosity with the Expected Porosity for the Polycrystalline UO_2 Disk/Molten Zry System. ($T=1900\text{ }^{\circ}\text{C}$, $t=120\text{s}$)

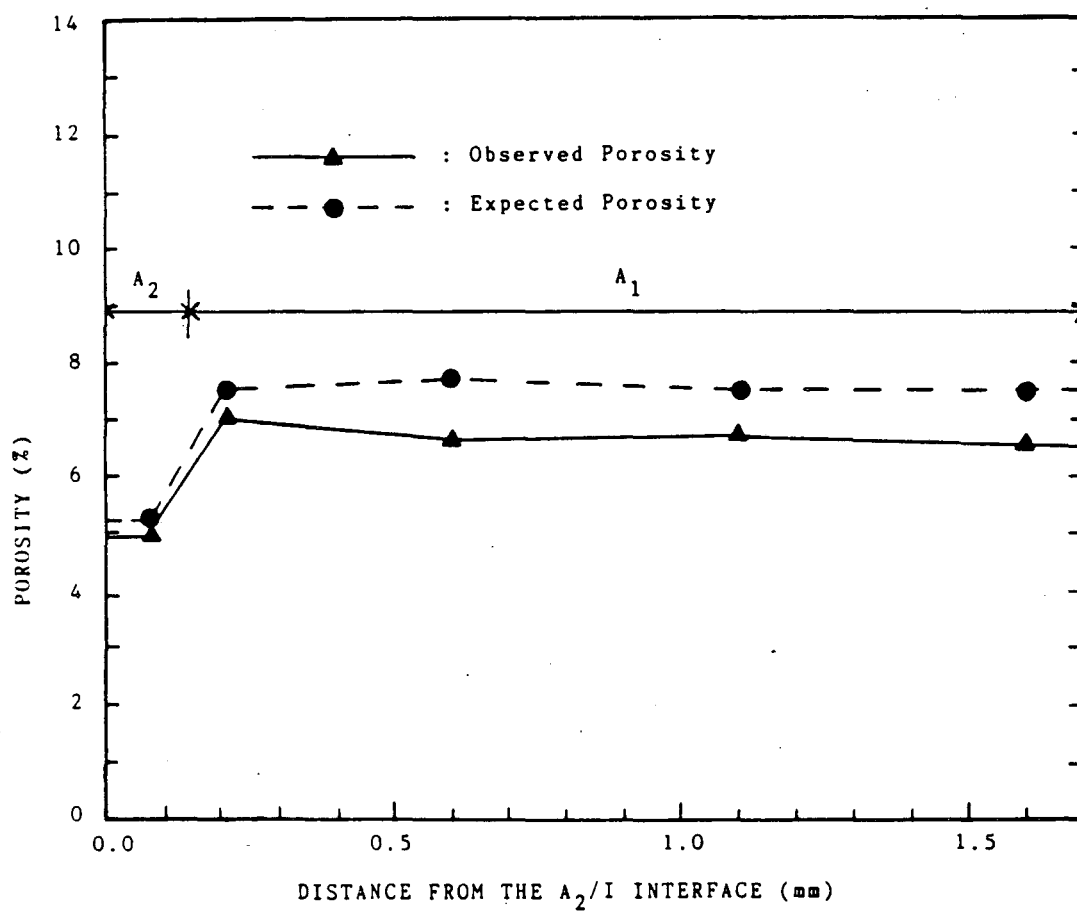


Fig.4.11 Comparison of the Observed Porosity with the Expected Porosity for the Polycrystalline UO₂ Disk/Molten Zry System.(T=2000 °C, t=205s)

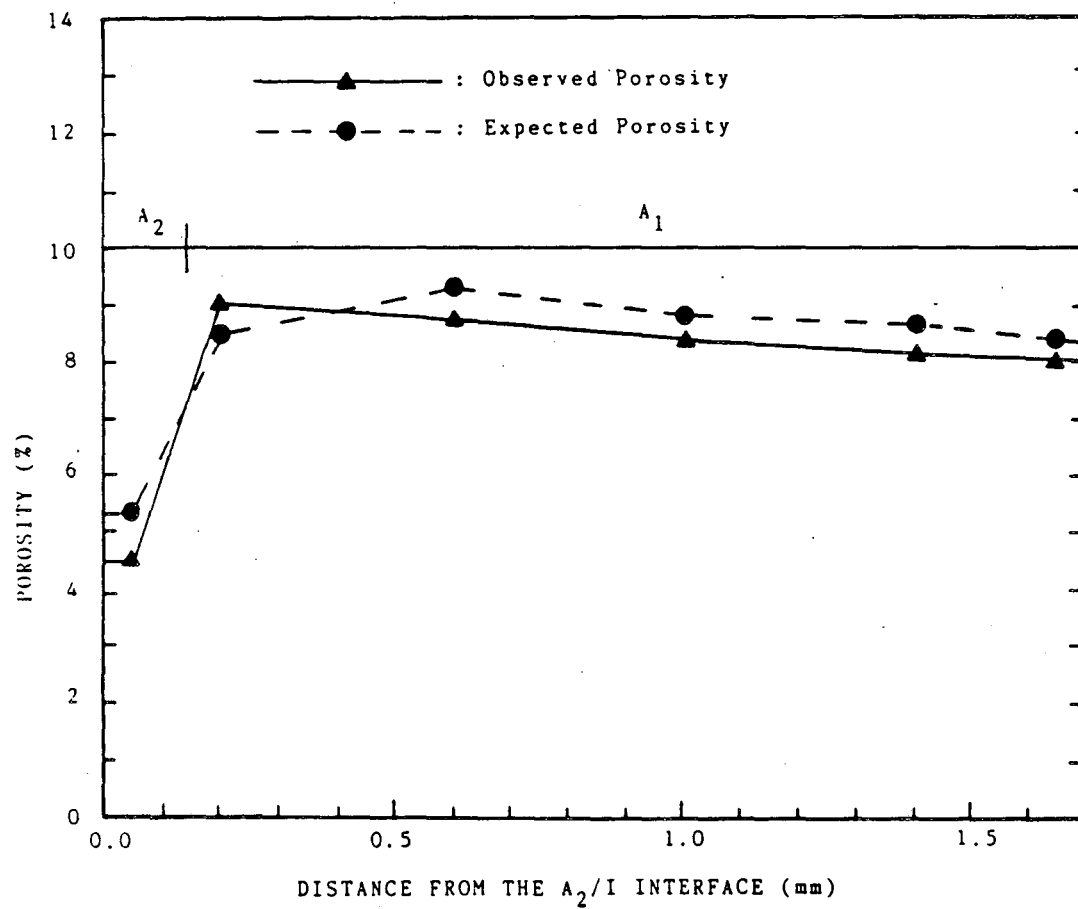


Fig. 4.12 Comparison of the Observed Porosity with the Expected Porosity for the Polycrystalline UO_2 Disk/Molten Zry System. ($T=2100\text{ }^{\circ}\text{C}$, $t=120\text{s}$)

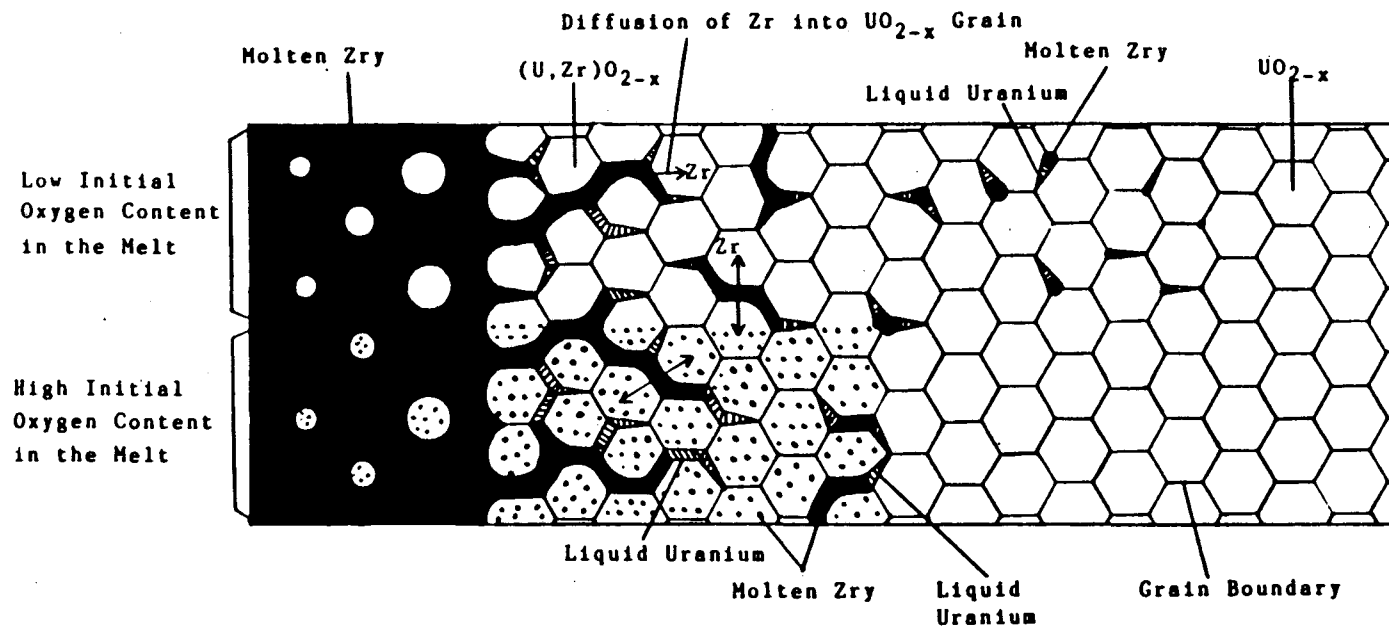


Fig.4.13 A Schematic Diagram of the Dissolution Mechanism of Polycrystalline UO_2 .

boundaries, however, the molten Zry further reduces UO_{2-x} to $UO_{2-x'}$ plus liquid uranium along the grain boundaries of UO_{2-x} in direct contact with the molten Zry. The molten Zry penetrates into the interior along liquid uranium on the grain boundaries to form the (U,Zr,O) channels and Zr^{4+} diffuses into the UO_{2-x} grains to form the (U,Zr) O_{2-x} solid solutions. Consequently, the porous-medium-like structure, the channel structure and the separate particles of (U,Zr) O_{2-x} (all characteristic of region I) appear in the microstructure. In addition, the size of the remaining (U,Zr) O_{2-x} solid surrounded by the circular shapes of α -Zr(O) particles near the A_2/I interface is about the grain size of the original UO_2 . Finally, the separate particles of (U,Zr) O_{2-x} become smaller with increasing distance from the interface as they are dissolved in the oxygen-poor Zry melt.

Similarly, at a relatively high initial oxygen content of the Zry, the molten Zry reduces UO_2 to UO_{2-x} with no oxygen gradient through the UO_2 disk. The molten Zry further reduces UO_{2-x} to $UO_{2-x'}$ plus liquid uranium along subgrain boundaries or dislocations as well as grain boundaries. The molten Zry penetrates through this liquid uranium to form (U,Zr,O) channels and Zr^{4+} diffuses into the UO_{2-x} grains to form the (U,Zr) O_{2-x} solid solutions. Consequently, the porous-medium-like structure mixed with the channel structure and the separate particles of (U,Zr) O_{2-x} appear in the microstructure. However, the extent of UO_2 reduction and the fraction of the (U,Zr) alloy precipitated from the (U,Zr,O) channels are much smaller than those at a low initial oxygen content of the Zry. In addition, the size of the remaining (U,Zr) O_{2-x} solid surrounded by the circular shapes of α -Zr(O) particles is much less than the grain size of the original UO_2 .

Hofmann et al(8) reported that the dissolution of polycrystalline UO_2 by molten Zry resulted in a sudden disintegration of the solid UO_2 and argued that this phenomenon is probably due to liquid uranium formed along the UO_2 grain boundaries which are not in contact with the molten Zry. In the present work, however, there was no wide-spread disintegration of the UO_2 disk and liquid uranium channels were not observed in regions A_1 and A_2 (solid oxide). In addition, it is more likely that liquid uranium channels form first along

the UO_2 grain boundaries in direct contact with the molten Zry than along the grain boundaries not in contact with the molten Zry. Subsequently, these liquid uranium channels move into the UO_{2-x} solid along the grain boundaries due to the especially rapid loss of oxygen along them. As a result, the liquid uranium appearing inside the UO_2 should be connected to the bulk molten Zry.

B) Reaction Kinetics

The diffusion coefficient of a solute in a melt is a fundamental quantity required to characterize the mass-transport rate. The number of liquid systems studied and the values of the diffusion coefficients measured therein represent only a small fraction of the number of determinations in the solid state. The reason for this paucity of data is the numerous serious difficulties in accurately measuring diffusion coefficients in liquid metals at elevated temperatures. The main difficulty is to avoid a mass transport by natural convection. This bulk motion of fluid is driven by buoyancy forces produced by either temperature or concentration gradients. The extent of these difficulties varies with the type of method and the experimental technique used(34, 35, 36, 37). Of the various methods, the majority of the diffusion coefficients that have been measured for molten metals have been obtained by using capillary methods. The polycrystalline UO_2 disk/molten Zry system used here(Fig. 2.4-a) is an example of the method by which the solid phase is allowed to come into contact with the melt over a broad area.

The growth rates of the diffusion zone are shown in Figs. A.1 through A.10. The growth kinetics of the individual layers obey the parabolic law. The individual layers growth rate constants are plotted versus reciprocal temperature in Arrhenius fashion(Figs. A.14 through A.16). These figures indicate that the kinetics of the growth of the various layers are thermally-activated.

A schematic diagram of the reaction layer movements is shown in Fig. 4.14. The interfaces in this figure do not exist at the reaction temperature but nevertheless represent the

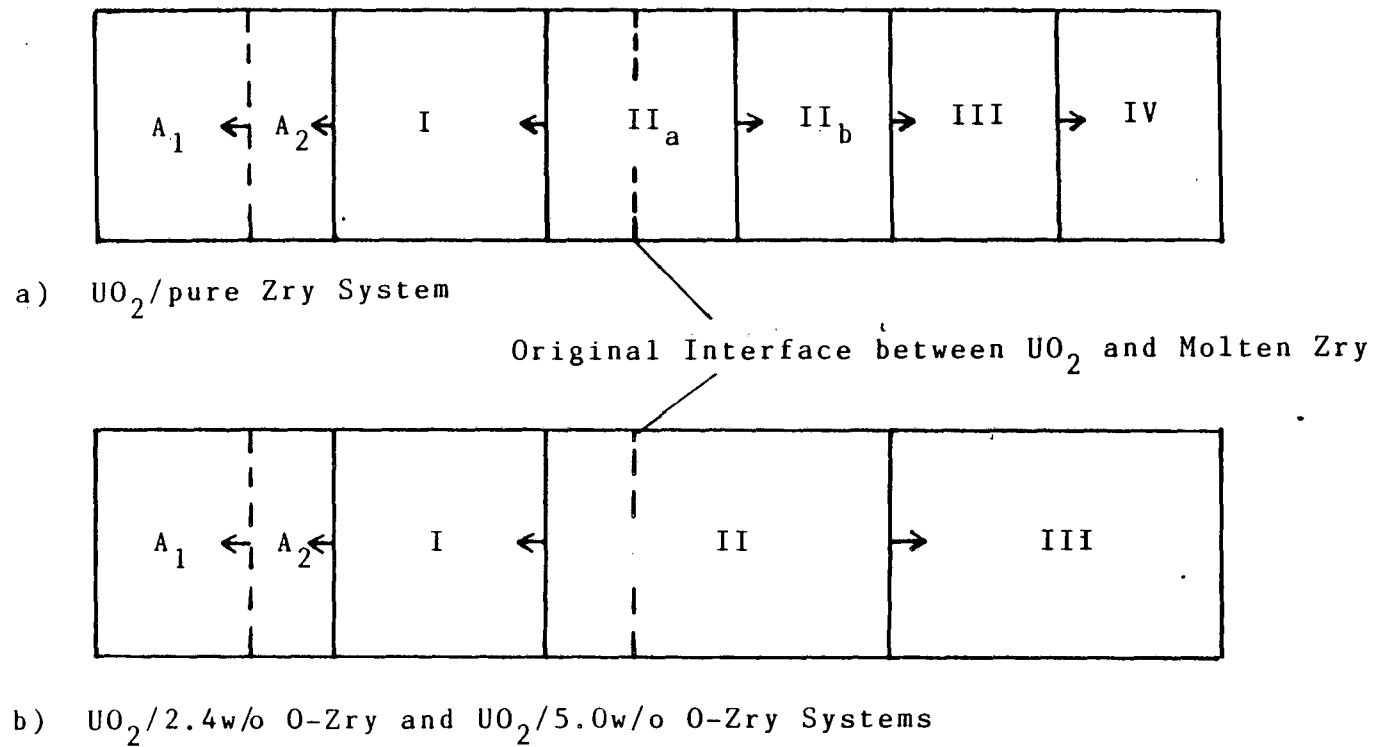


Fig.4.14 A Schematic Diagram of Reaction Layer Movement
for the UO₂ Disk/Molten Zry System.

penetration of uranium and oxygen into the molten Zry. Only the simple layers shown in Fig. 4.1 exist at reaction temperature. Fig. 4.14 shows that the growth of region I is governed by movement of the A_2/I and the I/II interfaces. As explained in section 4.2.2, the former represents the penetration front of the molten Zry along the grain boundaries and/or the subgrain boundaries of UO_2 . On the other hand, the latter is governed by the dissolution rate of the separate $(U,Zr)O_{2-x}$ particles by the molten Zry. The activation energy for the growth rate of region I, therefore, is determined by the combined effects of the penetration of the molten Zry into solid UO_{2-x} and the complete dissolution of the separate $(U,Zr)O_{2-x}$ particles by the liquid melt by which they are surrounded.

The growth of region II is controlled by movement of the I/II and II/III interfaces. As explained above, the former represents the dissolution rate of the separate $(U,Zr)O_{2-x}$ particles by the melt. On the other hand, the latter is governed by the uranium diffusion in the molten Zry. Therefore, the activation energy of a parabolic rate constant is equal to that of $D_u \Delta C_u$, where D_u is the uranium diffusion coefficient in molten Zry and ΔC_u is uranium concentration driving force (i.e., C_{su} at the I/II interface for this work). Fig. A.19 shows that the growth rate of region II decreases as the initial oxygen content of the Zry increases. The activation energies of parabolic rate constants, however, are nearly independent of the initial oxygen content of the Zry.

The growth rate of region III for the UO_2 /pure Zry system may be controlled by the diffusion of oxygen in the molten Zry, because the oxygen content of nearly uranium-free Zry dictates whether the α or β phase is stable at low temperature. The activation energy for the growth rate of region III may correspond to the activation energy of oxygen diffusion in molten Zry. However, there has been no investigation which can be compared directly with the present work. In general, it is believed that the activation energy of oxygen diffusion in liquid metals does not depend strongly on the particular metal. The activation energies of oxygen in molten systems are shown in Table 6. The considerable disagreement between different investigators reflects the difficulty in obtaining accurate measurements at high tem-

Table 6 Diffusion coefficients of oxygen in molten system

Oxygen source	Molten system	Temperature (°C)	D=D ₀ exp(-E/RT)		Method*	Ref.
			D ₀ (cm ² /s)	E(kcal/mole)		
O(UO ₂)	Zircaloy	1900 - 2100	1.2 x 10 ⁻¹	38	R	Present work
O(SiO ₂)	Fe	1550 - 1680	3.3 x 10 ⁻³	12	RD	38
O	Fe	1560 - 1660	5.5 x 10 ⁻³	20	C	39
O	Fe-Ti	1530 - 1700	6.2 x 10 ⁻³	11	RD	40
O	Fe	1550 - 1660	5.2 x 10 ⁻²	25	RD	41
O (Fe-0.07 O)	Fe-C	1550 - 1650	2.9 x 10 ⁻³	9	RD	42

* C : Capillary

RD : Rotating Disk

R : Planar Diffusion(This Work)

peratures. The activation energy of a parabolic rate constant is equal to that of $D_o \Delta C_o$, where D_o is the oxygen diffusion coefficient in molten Zry and ΔC_o is oxygen concentration driving force (i.e., C_{sat}^o at the I/II interface for this work).

The amount of UO_2 dissolved at saturation depends on molten Zry volume, an initial oxygen content of molten Zry, and temperature. In addition, the parabolic rate constant of the UO_2 dissolution depends on temperature and the ratio of molten Zry volume to UO_2 surface area in contact with molten Zry. However, the parabolic rate law for the UO_2 dissolution is applicable only if the molten Zry volume is relatively large or reaction time is relatively short (a semi-infinite Zry system). In the present work, a semi-infinite molten Zry system appears to apply because the parabolic rate constant for the UO_2 dissolution is independent of reaction time (Figs. A.11 through A.13). In order to model the parabolic rate law of for the UO_2 disk dissolution, the fractional dissolution of the UO_2 disk is calculated by using the one-dimensional diffusion analysis for a semi-infinite system, in which the rate-controlling step is assumed to be the uranium diffusion in molten Zry. The detailed calculations are given in Appendix C. The experimental data for the UO_2 disk dissolution (ΔL_x) are normalized by the maximum decrease of the UO_2 disk thickness (ΔL_∞). ΔL_∞ is calculated in Appendix C. Comparison of the normalized experimental data with the calculated curve is shown in Fig. 4.15. In this figure, the upper limit of the normalized experimental data is determined by considering region I to be dissolved (i.e. ΔL_x in Fig. A.1), while the lower limit is determined by considering region I to be undissolved. Note that regions I contains uranium which is partially dissolved, as explained in section 3.1.3. Comparison of the experimental data with the calculated curve shows good agreement, justifying the notion that the UO_2 disk dissolution is controlled by the uranium diffusion in the molten Zry.

Fig. A.17 shows that the parabolic rate constants decrease and the activation energies increase as the initial oxygen content of the Zry increases. These phenomena are probably due to the dependence of $(U,Zr)O_{2-x}$ solubility in molten Zry on temperature. From the quasi-binary section between α -Zr(O) and UO_2 (Fig. 1.2), it is thought that $(U,Zr)O_{2-x}$ solubil-

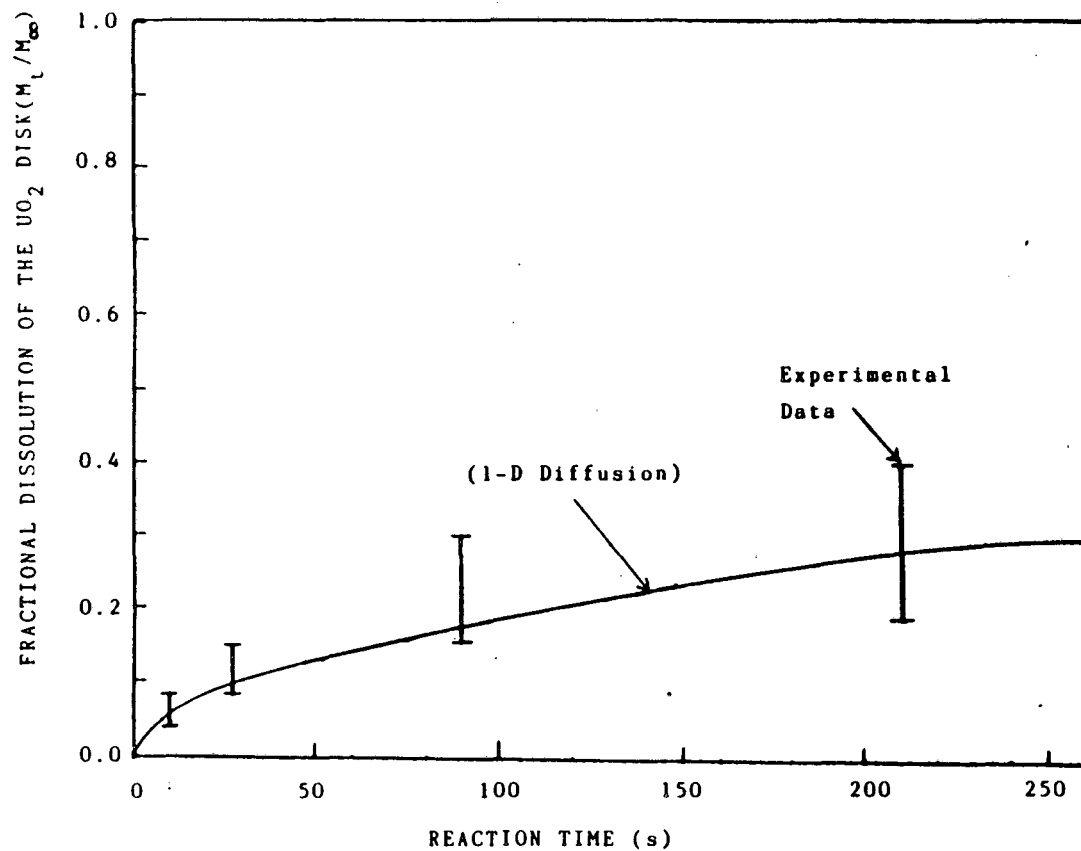


Fig.4.15 Fractional Dissolution of the UO_2 Disk for the UO_2 Disk/Pure Zry Reactions at 2000°C as a Function of Reaction Time Modeled as a Semi-infinite One-dimensional Diffusion Process.

ity in molten α -Zr(O) increases rapidly as temperature increases. Therefore, the extent of the $(\text{U,Zr})\text{O}_{2-x}$ solubility reduction, which is caused by the high initial oxygen content of the molten Zry, becomes smaller as temperature increases. Consequently, the effects of the initial oxygen content of the molten Zry on the UO_2 dissolution rate constants become smaller as reaction temperature increases.

4.2.3 Polycrystalline UO_2 Crucible/Molten Zry System

A) Transport Mechanism

Fig. 3.43 shows that most of the UO_2 dissolution takes place mostly during the incubation period, which cannot be rationalized by uranium diffusion in molten Zry. In order to model this observation, the fractional dissolution of uranium in region II is calculated for two limiting cases : a) uranium transport by natural convection and b) uranium diffusion in molten Zry. The detailed calculations are given in Appendix D. The experimental data shown in Fig. 3.43 are normalized by the saturation concentration of uranium of molten Zry. From Eq. (G.5), the saturation concentration at 2200 °C is 78 w/o. Comparison of the experimental data with the calculated curves is shown in Fig. 4.16. This figure shows that, at short reaction times, the experimental data agree satisfactorily to the natural convection curve. However, at long reaction times, the natural convection curve overestimates the fractional dissolution of uranium. This overestimation can be explained as follow. The natural convection curve shown in Fig. 4.16 was calculated by considering buildup of U in the bulk melt but assuming constant viscosity. Solid $(\text{U,Zr})\text{O}_{2-x}$ particles, however, appeared in region II just after the incubation period(Fig. 3.20) and then were accumulated with an increase of reaction time(Fig. 3.44). In addition, it was reported that solid particles in fluid increase the effective viscosity of fluid(46), which results in an additional decrease in the extent of natural convection with an increase of reaction time.

From Fig. 4.16, it was found that the UO_2 crucible dissolution during the incubation

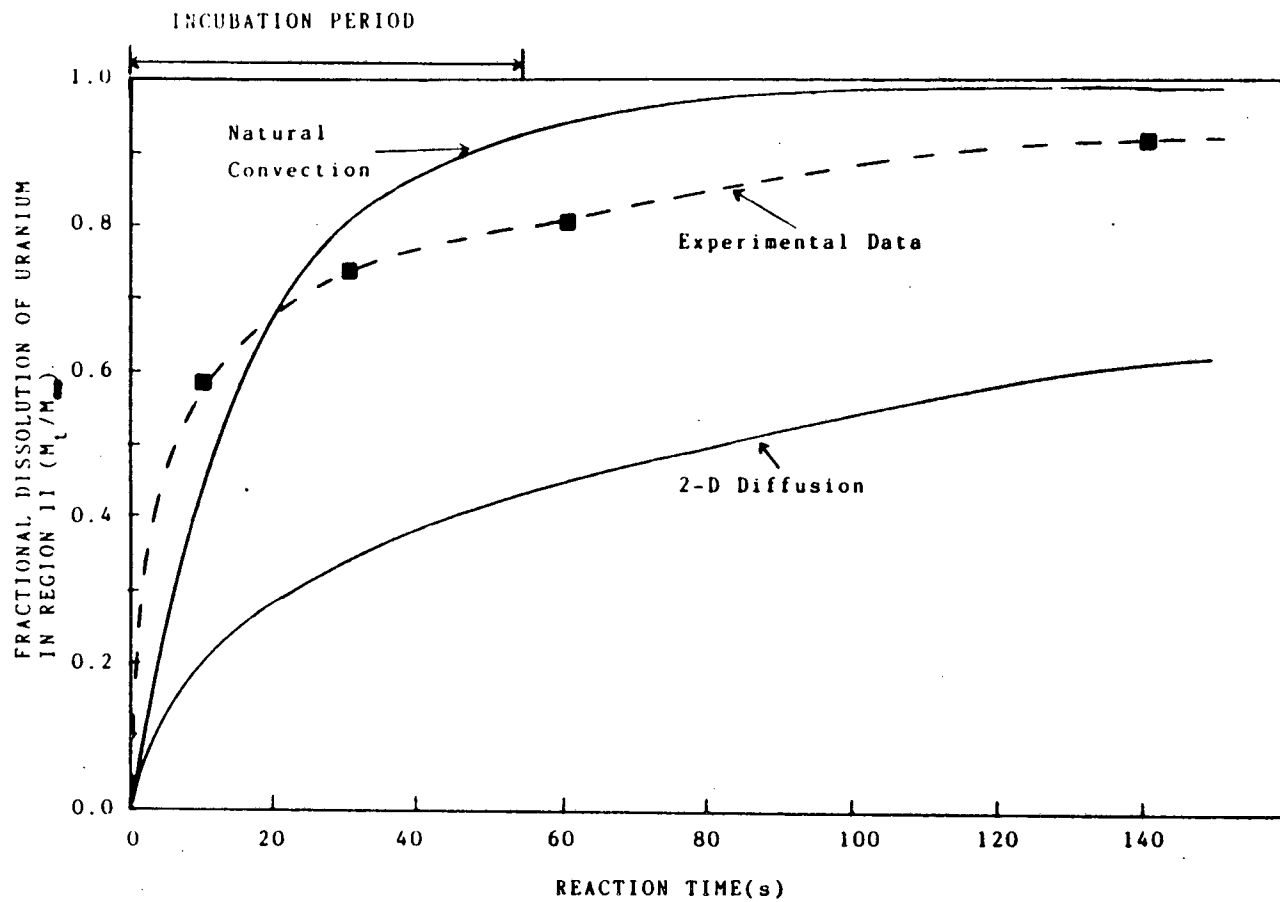


Fig.4.16 Fractional Dissolution of Uranium in Region II for the UO_2 Crucible/Pure Zry Reactions at 2200 °C as a Function of Reaction Time.

period, which is represented by the A_2/II interface movement, is controlled by the uranium transport by natural convection. In order to explain the uranium transport by natural convection, a qualitative flow motion caused by a density gradient is sketched in Fig. 4.17, which is based on the flow pattern caused by a temperature gradient (see Figs. 1.5 and 1.6). The flow field shown in Fig. 4.17-a can be divided into three regions, as explained in section 1.3: a boundary layer along the UO_2 crucible/molten Zry interface, a mixing region at the bottom and a central main core. The dense fluid in the vicinity of the wall descends in the boundary layer. On reaching the bottom of the crucible, it flows toward the center of the crucible, disperses and mixes, and returns as an upward motion of the dense fluid. The axial velocity distribution in the momentum boundary layer (Fig. 4.17-b) starts at zero at the wall and rapidly grows to its maximum value, and slowly returns to zero at a position, which defines the thickness of the momentum boundary δ_m . The main core rises with a plug velocity. On the other hand, the concentration is a maximum at the wall (C_{su}) and shortly drops to the bulk concentration (C_{bu}) over a distance, which defines the thickness of the concentration boundary δ_c . According to Eq. (1.7) in section 1.3, an increase of viscosity or a decrease of uranium concentration difference across the concentration boundary layer (ΔC_u) decreases the Raleigh number. In the present work, ΔC_u decreases with an increase of reaction time even in the absence of a change in the effective viscosity of the liquid, since there are no solid particles in the liquid during the incubation period. In addition, it is generally believed that δ_c is proportional to δ_m and that δ_c and δ_m increase as the Raleigh number decreases, according to Eq. (1.5) in section 1.3. A decrease of the Raleigh number with an increase of reaction time, therefore, results in a decrease in the extent of natural convection, which reduces the rate of uranium transport through the concentration boundary layer. These processes of natural convective-transport are extremely complex and presently not well understood. In addition, the incubation period is too short to determine reaction kinetics quantitatively.

For reaction times after the incubation period, dissolution of the $(U,Zr)O_{2-x}$ particles

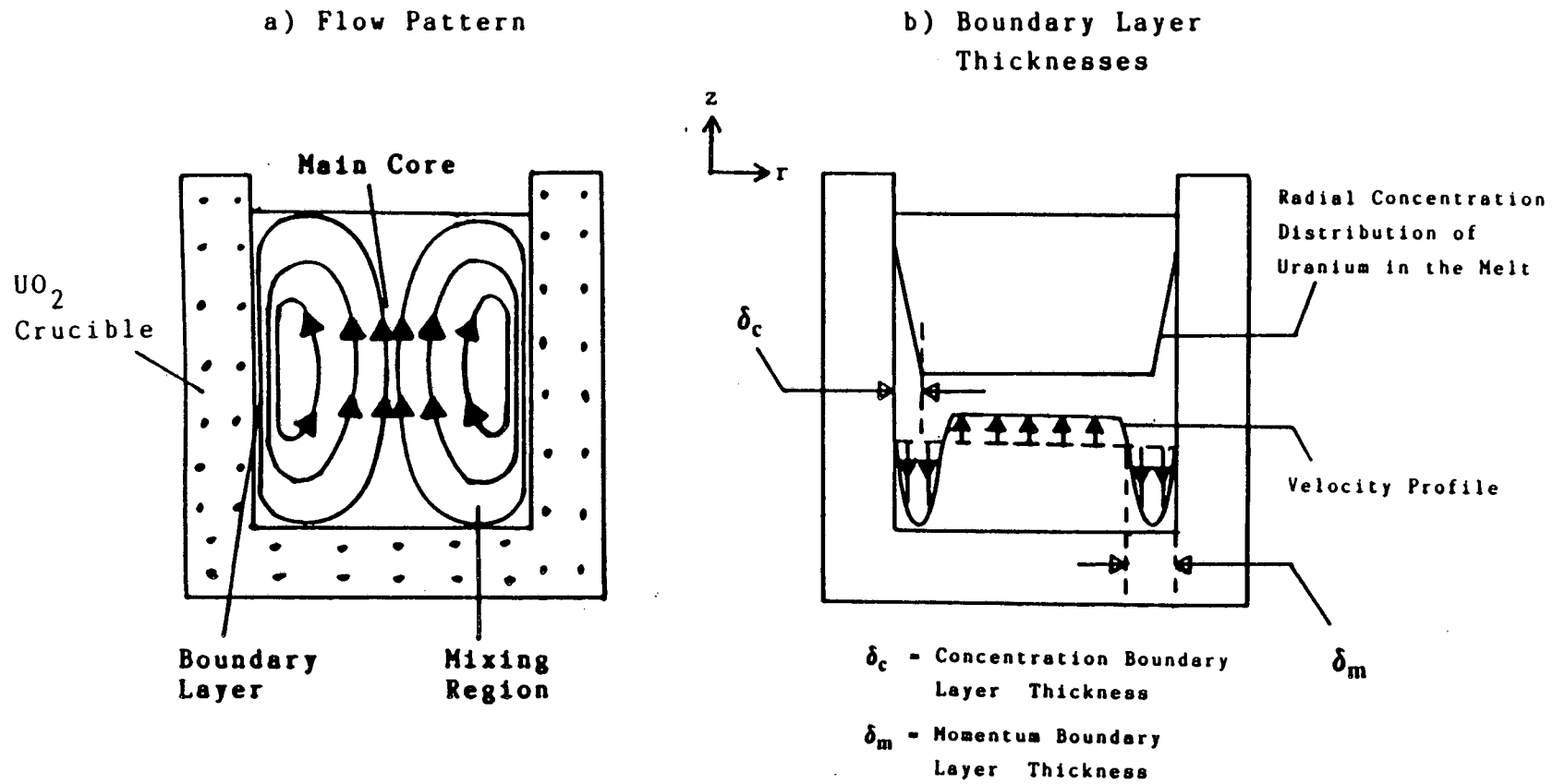


Fig. 4.17 Qualitative Flow Pattern and Boundary Layer Thicknesses Caused by a Density Gradient in the Melt.

dispersed in region II becomes more difficult because the oxygen content in region II (molten region) increases as the $(\text{U,Zr})\text{O}_{2-x}$ particles are dissolved. In addition, the effective viscosity of the melt increases with the accumulation of the $(\text{U,Zr})\text{O}_{2-x}$ particles in the molten region. This results in an additional decrease in the extent of natural convection, as explained above. This assertion is supported by the distribution of the $(\text{U,Zr})\text{O}_{2-x}$ particles in region II (Fig. 4.18), which shows that the amount of the $(\text{U,Zr})\text{O}_{2-x}$ particles decreases on moving upward. Note that the density of $(\text{U,Zr})\text{O}_{2-x}$ is higher than that of liquid Zry, so some gravitational settling takes place. During the incubation period, however, the concentration of uranium in region II appears to be uniform in the axial direction. Consequently, after the incubation period, uranium transport by the diffusion mechanism becomes effective and thus the dispersion of the $(\text{U,Zr})\text{O}_{2-x}$ particles next to the solid-melt interface is retarded, which causes the formation of region I.

In order to confirm the effect of the oxygen content of region II on the formation of region I, the UO_2 crucible/6.0w/o O-Zry system was tested at 2100 °C for various times. Figs. 3.40 and 3.41 show that there is a negligible incubation period. In addition, Fig. 3.43 shows that the amount of UO_2 dissolved and the UO_2 dissolution rate for the 6.0w/o O-Zry are much smaller than those for the pure Zry at 2100 °C. It is, therefore, emphasized that the amount of UO_2 dissolved at saturation, the UO_2 dissolution rate and the incubation period depend strongly on the initial oxygen content of the molten Zry and reaction temperature.

Region I appears after the incubation period, as explained above. Figs. 3.35 through 3.40 show that the incubation period becomes longer and the amount of uranium dissolved during the incubation period increases with an increase of reaction temperature. These phenomena are probably due to the dependence on reaction temperature of $(\text{U,Zr})\text{O}_{2-x}$ solubility in molten Zry and of melt viscosity. Fig. 1.2 shows an increase of $(\text{U,Zr})\text{O}_{2-x}$ solubility in $\alpha\text{-Zr(O)}$ with an increase of temperature, which results in an increase of the uranium concentration difference of the concentration boundary layer (ΔC_u). In addition, it is well-

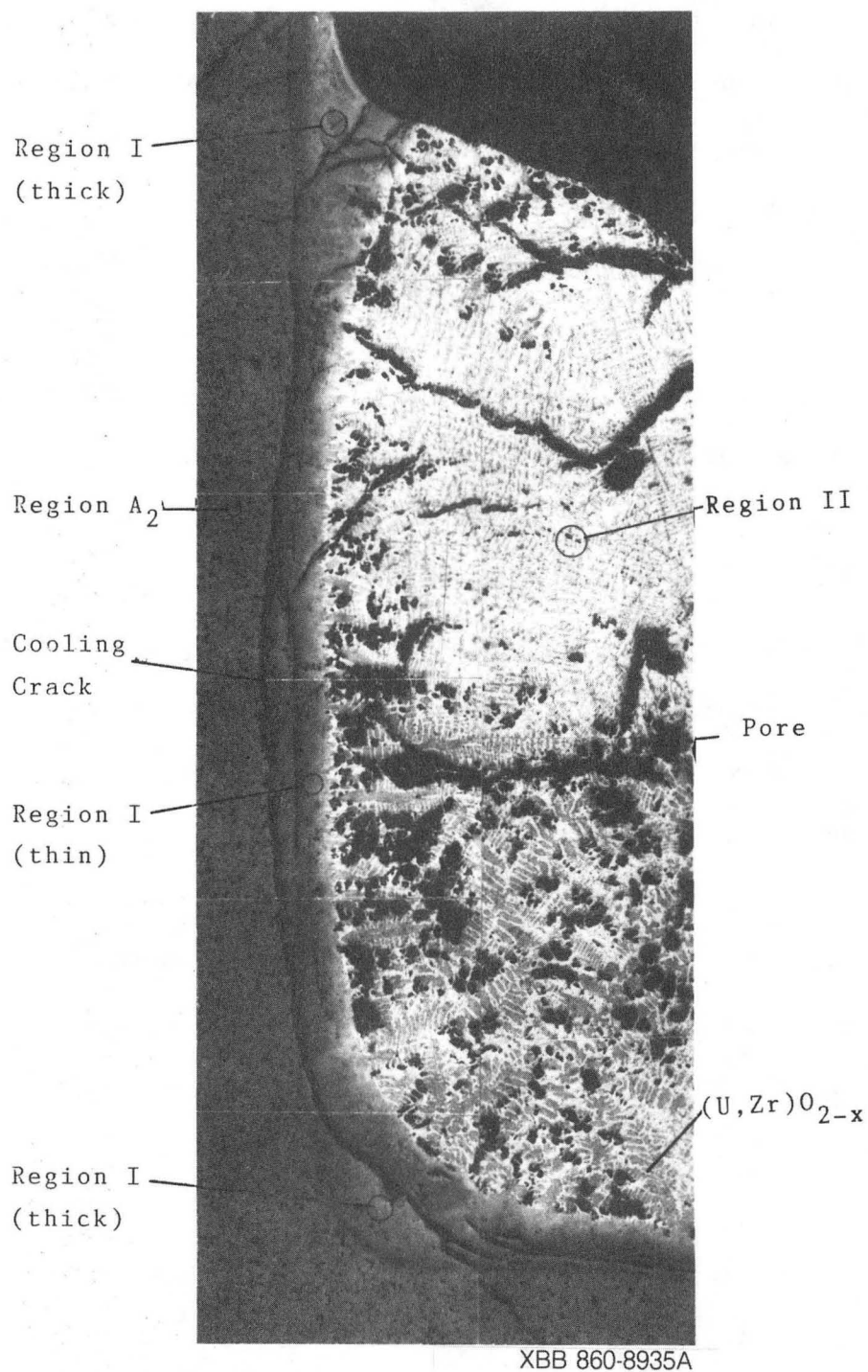


Fig.4.18 Variation of Region I Thickness for UO₂ Crucible/
Molten Zry System(Optical). (T=2050 °C, t=480 s)

known that viscosity decreases exponentially with an increase of temperature. As explained above, the smaller viscosity and the higher ΔC_u with an increase of reaction temperature cause a stronger natural convection, which retards the formation of region I. The incubation period, therefore, is longer and the amount of uranium dissolved during the incubation period is larger as reaction temperature increases.

B) Dissolution Mechanism of the Solid Polycrystalline Oxide

The probable microscopic mechanism of UO_2 crucible dissolution is described as follows. During the incubation period, the UO_2 crucible is rapidly reduced to UO_{2-x} by oxygen uptake by the oxygen-poor molten Zry. Because of oxygen removal from the UO_2 crucible, liquid uranium is formed along the grain boundaries of UO_{2-x} in contact with the molten Zry. Subsequently, the molten Zry penetrates through this liquid uranium on the grain boundaries and some of the penetrating zirconium diffuses into the UO_{2-x} grains to form the $(U,Zr)O_{2-x}$ solid solutions. The same microstructure as region I for the polycrystalline UO_2 disk/pure Zry (see Fig. 3.5), therefore, has a tendency to form at the UO_2 crucible/molten Zry interface. During the incubation period, however, a strong natural convection exists in the UO_2 crucible/molten Zry system, as explained above. As a result, the complex structure of region I, which might have remained at the UO_2 crucible/molten Zry interface (i.e., the A_2/II interface) in the absence of natural convection, is dispersed by the convective motion and easily dissolved in the oxygen-poor molten Zry (region II). The subsequent dissolution of the UO_{2-x} crucible after the incubation period, however, is more difficult because the oxygen content of the melt is high and the extent of natural convection is considerably decreased. It is, therefore, likely that, after the incubation period, the molten Zry reduces UO_{2-x} to UO_{2-x} plus liquid uranium along the subgrain boundaries or dislocations as well as the grain boundaries. Then, the molten Zry penetrates through this liquid uranium to form the salient microstructure of region I (Fig. 3.25). This figure shows that region I has the porous-medium-like structure near the A_2/I interface and the channel

structure mixed with the porous-medium-like structure near the I/II interface. These microstructural features are essentially the same as those of the polycrystalline UO_2 disk/5.0w/o O-Zry interface(Fig. 3.11).

C) Reaction Kinetics

A schematic diagram of the reaction layer movements is shown in Fig. 4.19. This figure indicates that, during the incubation period(Fig. 4.19-a), the A_2 /II interface moves radially outward. After the incubation period the interface movements depend on reaction temperature and the initial oxygen content of the Zry. For a relatively low temperature and high initial oxygen content of the Zry(Fig. 4.19-b), the I/II interface moves radially inward. For a relatively high temperature and low initial oxygen content of the Zry(Fig. 4.19-c), however, the I/II interface moves radially outward, but at a slower rate than the A_2 /I interface.

Fig. 4.18 shows that region I is much thicker at the corner and at the upper locations of the wall than at the vertical wall. This phenomenon can be explained as follows. The corner and the upper locations near the wall are inherently stagnant fluid zones. This results in less effective scouring of the partially liquid region I at these locations. Regions I at these locations, therefore, grow faster than of the side wall removed from the ends. On the other hand, the growth of region I is governed by the relative movement between the A_2 /I interface and the I/II interface(see Fig. 3.35 through 3.40). Based on the transport and the dissolution mechanisms, as explained above, it is thought that the A_2 /I and the I/II interface movements are controlled by two processes : a) penetration of molten Zry along the grain boundaries and/or the subgrain boundaries of UO_2 , as evidenced by the EMP detection of zirconium deep within the ceramic phases A_1 and A_2 and b) sweeping of $(\text{U,Zr})\text{O}_{2-x}$ chunks by convective motion(see Fig. 3.21).

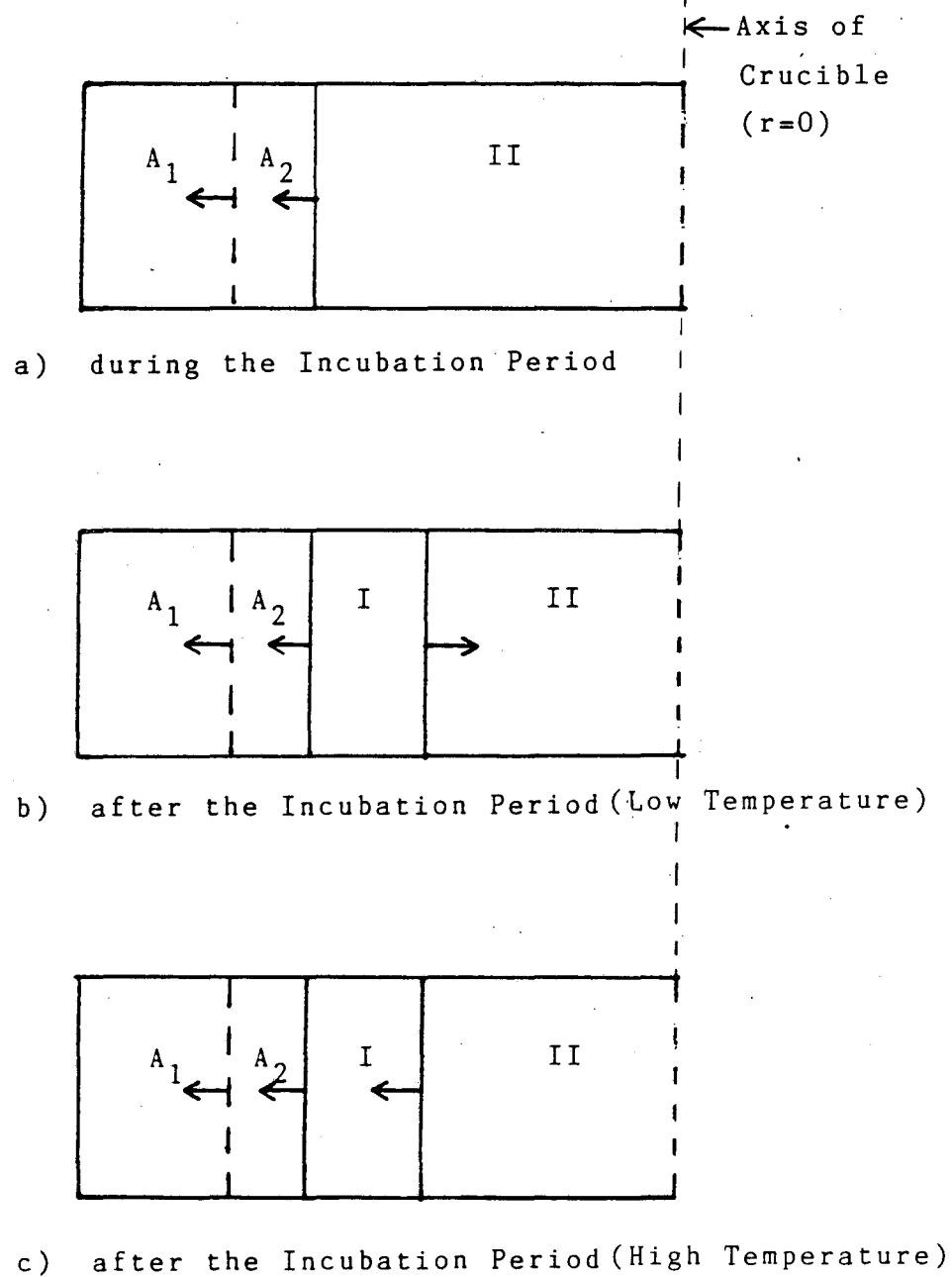


Fig.4.19 A Schematic Diagram of Reaction Layer Movement for the UO_2 Crucible/Molten Zry System.

4.3 Applicability of the Present Experimental Data to Severe Fuel Damage Situations

The UO_2 crucible design simulates more closely the vertical UO_2 surface with which the molten cladding is in contact during a melt-down event in reactor fuel than does the UO_2 disk geometry. Out-of-pile integral fuel rod and bundle tests at KfK(1) showed a uniform mixture of U, Zr, and O in the melt, which is consistent with the results of the present UO_2 crucible/molten Zry reactions. Therefore, the UO_2 crucible dissolution data obtained in the present work can be used as a first approximation to predict the melt-down behavior in reactor fuel, even though there are geometrical differences between the UO_2 crucible geometry and the reactor fuel on which the cladding has melted. Of particular significance is the ratio of the interface area(S) to the melt volume(V) in the two cases. For the present tests, $\frac{S}{V}$ is ~ 15 ; for a 0.7 mm thick cladding on a fuel pellet of 1 cm diameter, $\frac{S}{V}$ is also ~ 15 .

The results of the UO_2 crucible/molten Zry reactions(Fig. 3.43) show that most of the dissolution of UO_2 in the molten Zry occurs during the incubation period. Therefore, the UO_2 pellet dissolution for the melt-down event takes place mostly in a few minutes after contact of the UO_2 pellet by the molten Zry. On the other hand, for engineering-design calculations, interest is mainly concentrated on a determination of the maximum amount of UO_2 dissolved by molten cladding. Fig. 3.43 shows that the uranium concentration(on an oxygen-free basis) in the molten Zry closely approached saturation during the test times employed. From this figure, the saturation concentrations of uranium in the molten Zry were approximately estimated and plotted in Fig. G.2, as explained in Appendix G. In out-of-pile integral rod and bundle tests at KfK(1), it was found that the Zry cladding can be severely oxidized before melting. However, Fig. G.2 shows that the saturation concentration of uranium decreases significantly for the 6.0w/o O-Zry system. The amount of uranium dissolved by pure Zry, therefore, represents the maximum amount of uranium that can be dissolved by the molten cladding in a melt-down event.

Fig. 4.20 shows a plot of the fractional volume decreases of UO_2 pellet by molten Zry as

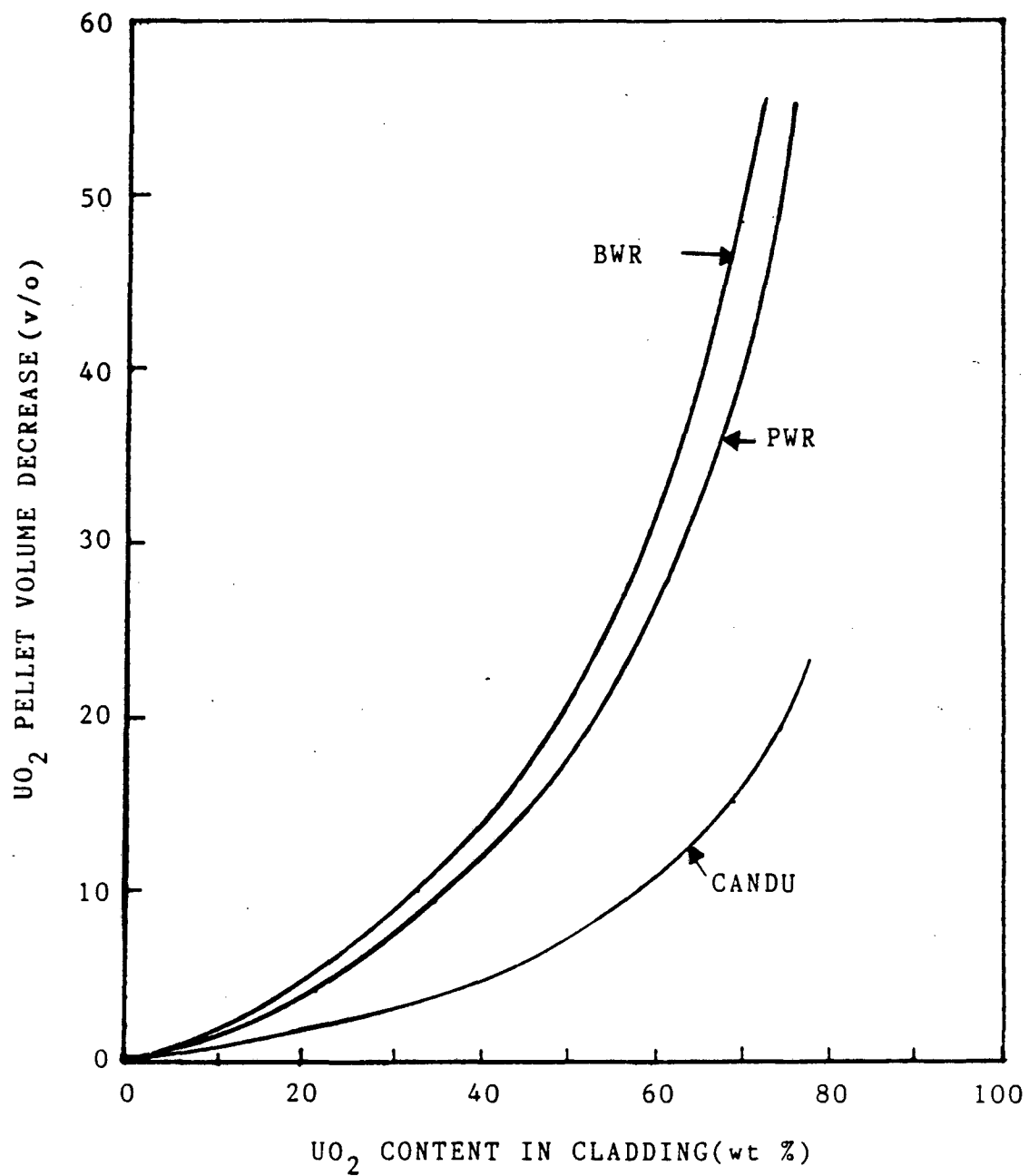


Fig.4.20 UO₂ Pellet Volume Decrease as a Function of UO₂ Content in Cladding for Three Typical Reactors.

a function of UO_2 content of molten cladding for three typical reactors. The detailed calculations are shown in Appendix E. This figure shows that fuel rods having smaller cladding volume (such as those in the CANDU reactor) can dissolve less UO_2 than the LWR fuel rods which have larger cladding volume. In addition, using Eq. (E.3) and Eq. (G.5) (the asymptotic saturation data), the maximum fractional volume decreases of UO_2 pellet by molten cladding for the three typical reactors are obtained at the reaction temperatures employed in the present work. The results are shown in Table 7. This table shows that, for the BWR reactor, the maximum volume decrease of pellet by pure Zry is as large as 31 % at 2100 °C, while that by 6.0 w/o O-Zry is as small as 6 % at 2100 °C. The cladding pre-oxidized by steam, therefore, will reduce drastically the amount of UO_2 pellet dissolved when cladding melting occurs.

While the maximum quantity of UO_2 liquefied depends on temperature, cladding volume, and an initial oxygen content of cladding, the rate at which saturation is approached (assuming that relocation does not occur) is a function of the $\frac{S}{V}$ ratio of the system (S = surface area of fuel in contact with cladding, V = volume of cladding associated with this surface). Barring gross displacement of the liquid cladding, a natural convection calculation of the type described in Appendix D will provide a conservative (i.e., overly rapid) estimate of the dissolution rate. Illustrative fuel liquefaction problems are solved in Appendix F

Table 7 Maximum UO_2 Pellet Volume Decrease(v/o) for Three Typical Reactors.

Initial Oxygen Content in Zry	Temperature (°C)	Max. Pellet Volume Decrease(v/o)		
		PWR	BWR	CANDU
Pure Zry (As-received)	1950	10	12	4
	2000	13	16	5
	2050	18	22	7
	2100	26	31	10
	2200	67	79	24
6.0 wt %	2100	5	6	2

5 CONCLUSIONS

Out-of-pile tests of the UO_2 /molten Zry reaction in inert gas(Ar-5% H_2) from 1900 to 2200 °C have been conducted. The conclusions are summarized as follows.

5.1 UO_2 Single Crystal/Molten Zry System

This system was designed to investigate the effects of the UO_2 grain boundaries(or, more precisely, their absence) on the reaction kinetics.

The UO_2 /Zry interface shows preferential attack by the molten Zry near surface regions of the UO_2 crystal. This attack forms $(\text{U,Zr})\text{O}_{2-x}$ particles and a porous medium-like structure of the partially dissolved $(\text{U,Zr})\text{O}_{2-x}$. This phenomenon indicates that concentration perturbations arising from the loss of oxygen from the UO_2 region cause liquid uranium to form within the crystal, possibly along the subgrain boundaries in contact with the molten Zry. Subsequent penetration of the molten Zry along this liquid uranium interlayer accelerates the formation of liquid uranium within the UO_2 bulk region. Zirconium is a more powerful reducing agent than uranium, and in addition, ingress of zirconium enlarges the liquid interlayer thickness, thus enhancing oxygen transport to the melt along this path.

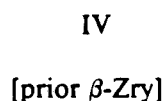
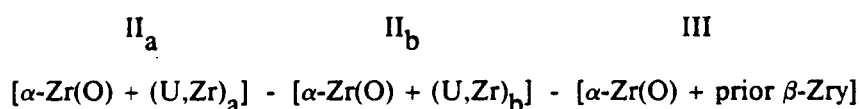
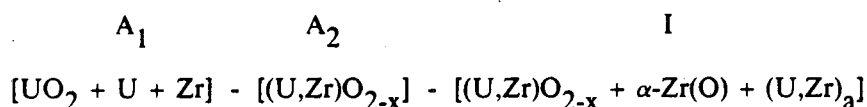
The solid oxide exhibits two distinct regions, $(\text{U,Zr})\text{O}_{2-x}$ (region A_2) and $(\text{UO}_2 + \text{U})$ (region A_1). Region A_2 , which is adjacent to the UO_2 /molten Zry interface, has very few pores and metal precipitates because zirconium stabilizes UO_{2-x} even at room temperature. In Zr-free region A_1 , however, the uniformly-distributed pores and uranium precipitates appeared due to the density change from the decomposition of UO_{2-x} to $[\text{UO}_2 + \text{U}]$. The uranium precipitates are mostly associated with the pores, probably due to the easy nucleation on the pore surface.

5.2 Polycrystalline UO_2 Disk/Molten Zry System

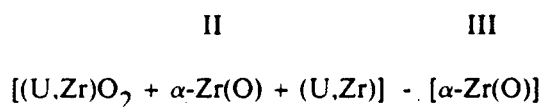
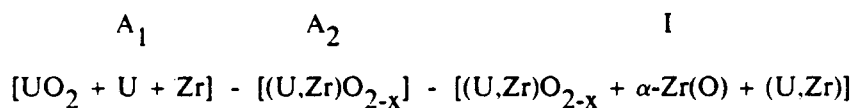
This system was designed to investigate the one-dimensional diffusion phenomena while suppressing natural convection of the melt.

The number and the sequence of reaction layers and products depend on the initial oxygen content of the Zry. For the same initial oxygen content of the Zry, however, they are the same for all temperatures and times tested.

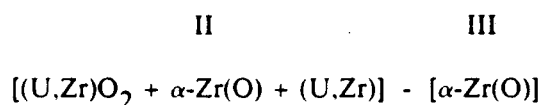
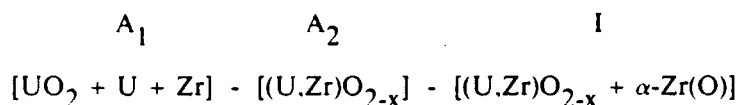
For the pure Zry, the room temperature sequence of the individual reaction layers is :



For the 2.4w/o O-Zry, the room temperature sequence of the individual reaction layers is :

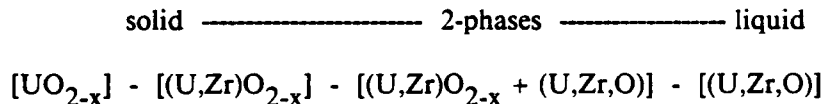


For the 5.0w/o O-Zry, the room temperature sequence of the individual reaction layers is :



The reaction layers and products at the reaction temperatures are explicable in terms of diffusion paths in the U-Zr-O phase diagram. These reaction layers and products are

independent of the initial oxygen content of the Zry and represented as follows.



Using the method of quenching to the freezing temperature (1500 °C) of the specimens tested in this work, the reaction layers and products observed in the postannealed specimen were reproduced by a diffusion path on the U-Zr-O isothermal section at 1500 °C.

The dissolution mechanism for the polycrystalline UO_2 disk/molten Zry system depends on the initial oxygen content of the Zry. For a relatively low initial oxygen content of the Zry, the dominant dissolution mechanism is the penetration of the molten Zry along the grain boundaries. As a result, the porous medium-like structure, the channel structure and the separate particles of $(\text{U,Zr})\text{O}_{2-x}$ (depending on the fraction of the UO_2 penetrated by the molten Zry) appear in the micrographs. For a relatively high initial oxygen content of the Zry, the dominant dissolution mechanism is the penetration of the molten Zry along the subgrain boundaries as well as the grain boundaries. Consequently, the porous medium-like structure mixed with the channel structure and the separate particles of $(\text{U,Zr})\text{O}_{2-x}$ appear in the micrographs.

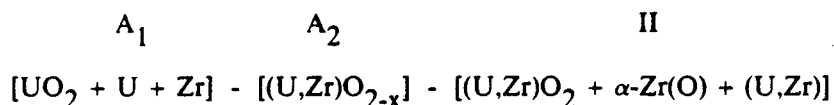
The $\alpha\text{-Zr(O)}$ particles, which are always found in pores, appear even near the bottom of the UO_2 disk. This phenomenon indicates that the preferential loss of oxygen along the grain boundaries may contribute to open porosity: the molten Zry then penetrates this open porosity.

In the temperature range examined, the layer-growth kinetics follow the parabolic rate law and the UO_2 dissolution was controlled by the uranium diffusion in molten Zry. However, as the initial oxygen content of the Zry increases, the amount of the UO_2 dissolution decreases and the activation energy for the dissolution rate increases. The latter phenomenon is probably due to the temperature dependence of $(\text{U,Zr})\text{O}_{2-x}$ oxide solubility in molten Zry.

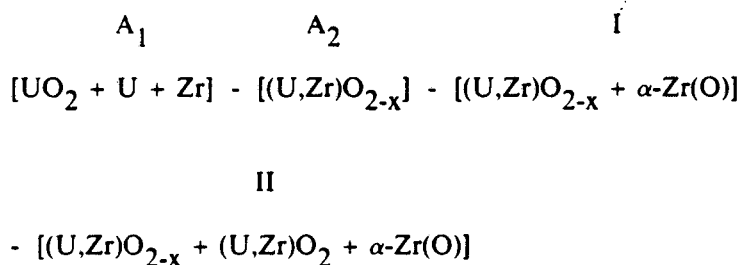
5.3 Polycrystalline UO_2 Crucible/Molten Zry System

This system was designed to simulate a melt-down phenomenon in reactor fuel by a vertical-dissolving-wall configuration which is conducive to natural convection in the melt. This fluid motion arises from density differences between the liquid near the crucible (rich in uranium) and the bulk liquid (principally zirconium).

The number and the sequence of reaction layers depend on reaction temperature, reaction time and the initial oxygen content of the Zry. For a relatively high temperature, short time and low initial oxygen content in the Zry, the room temperature sequence of the individual reaction layers is :



For a relatively low temperature, long time and high initial oxygen content of the Zry, the room temperature sequence of the individual reaction layers is :



Region I appears after an incubation period which increases as the reaction temperature increases and as the initial oxygen content of the Zry decreases. During the incubation period, the A_2/II interface moves radially outward, regardless of the reaction temperature and the initial oxygen content of the Zry. After the incubation period, the A_2/I and I/II interfaces movements are controlled by two processes : a) penetration of molten Zry along the grain boundaries and/or the subgrain boundaries of UO_2 and b) sweeping of $(\text{U,Zr})\text{O}_{2-x}$ chunks by convective motion. The absence of a diffusion-controlled process during this stage is indicated by no concentration gradients in the prior-molten zone. For a relatively

high temperature and low initial oxygen content of the Zry, the A_2/I and I/II interfaces move radially outward. For a relatively low temperature and high initial oxygen content of the Zry, however, the A_2/I interface moves radially outward and the I/II interface moves radially inward.

The dissolution mechanism for the polycrystalline UO_2 crucible/molten Zry system appears to be the same as that for the polycrystalline UO_2 disk/molten Zry system. During the incubation period, the oxygen content of the molten Zry is relatively low. The dominant dissolution mechanism, therefore, is the penetration of molten Zry along the grain boundaries. However, the multi-layered structure of the UO_2 crucible/molten Zry interface is destroyed by the strong convective motion, which is the dominant uranium-transport mechanism during the incubation period. After the incubation period, the oxygen and uranium contents of the molten Zry are relatively high, which reduces the driving force for fluid circulation. The dominant dissolution mechanism, therefore, switches to the penetration of molten Zry along the subgrain boundaries as well as the grain boundaries. The microstructural appearance of the UO_2 crucible/molten Zry interface is essentially the same as that of the UO_2 disk/5.0 w/o O-Zry interface.

Most of the dissolution UO_2 in molten Zry takes place during the incubation period, and only trace amount of UO_2 is dissolved after this period, especially at low temperature.

The saturation concentration of UO_2 in molten Zry depends on temperature and the initial oxygen content of the molten Zry. As temperature increases and the initial oxygen content decreases, the saturation concentration of UO_2 increases. Therefore, the saturation concentration for the present UO_2 crucible/pure Zry system represents the maximum amount of UO_2 that can be dissolved by molten Zry in a melt-down event. On the other hand, the rate at which the saturation concentration of UO_2 in the molten Zry is approached depends on the ratio of surface area of UO_2 in contact with molten Zry(S) to molten Zry volume(V). The larger value of $\frac{S}{V}$ gives the more rapid approach to saturation. Barring gross displacement of liquid Zry, however, the dissolution rate obtained from the present UO_2

crucible/molten Zry system will provide a conservative estimate for a melt-down event.

The concentrations of U, Zr and O indicate that more oxygen than uranium was extracted from the initially stoichiometric UO_2 crucible, thereby leaving the O/U ratio of the crucible less than 2 and the O/U ratio in the melt greater than 2. The asymptotic saturation concentrations of uranium in the melt were obtained and are found to have an Arrhenius dependence on temperature. The asymptotic saturation data are in qualitative agreement with the ternary phase diagram, and the difference from the pseudo-binary phase diagram is satisfactorily rationalized.

6 APPENDICES

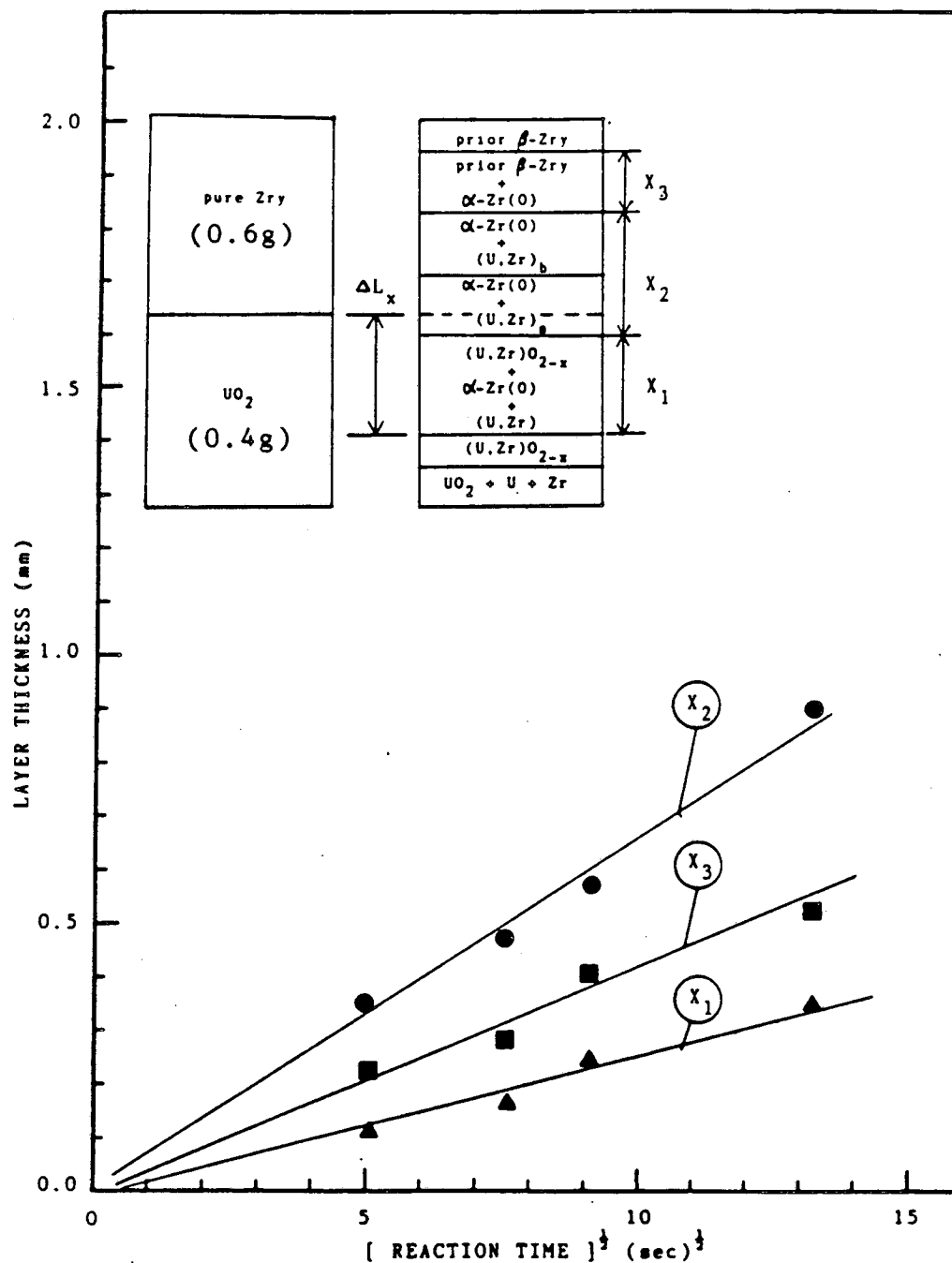
APPENDIX A : Figures for the UO_2 Disk/Molten Zry System

Fig. A.1 UO_2 /Pure Zry Reaction Zone Thickness versus $(\text{Reaction Time})^{1/2}$ at 2000 °C.

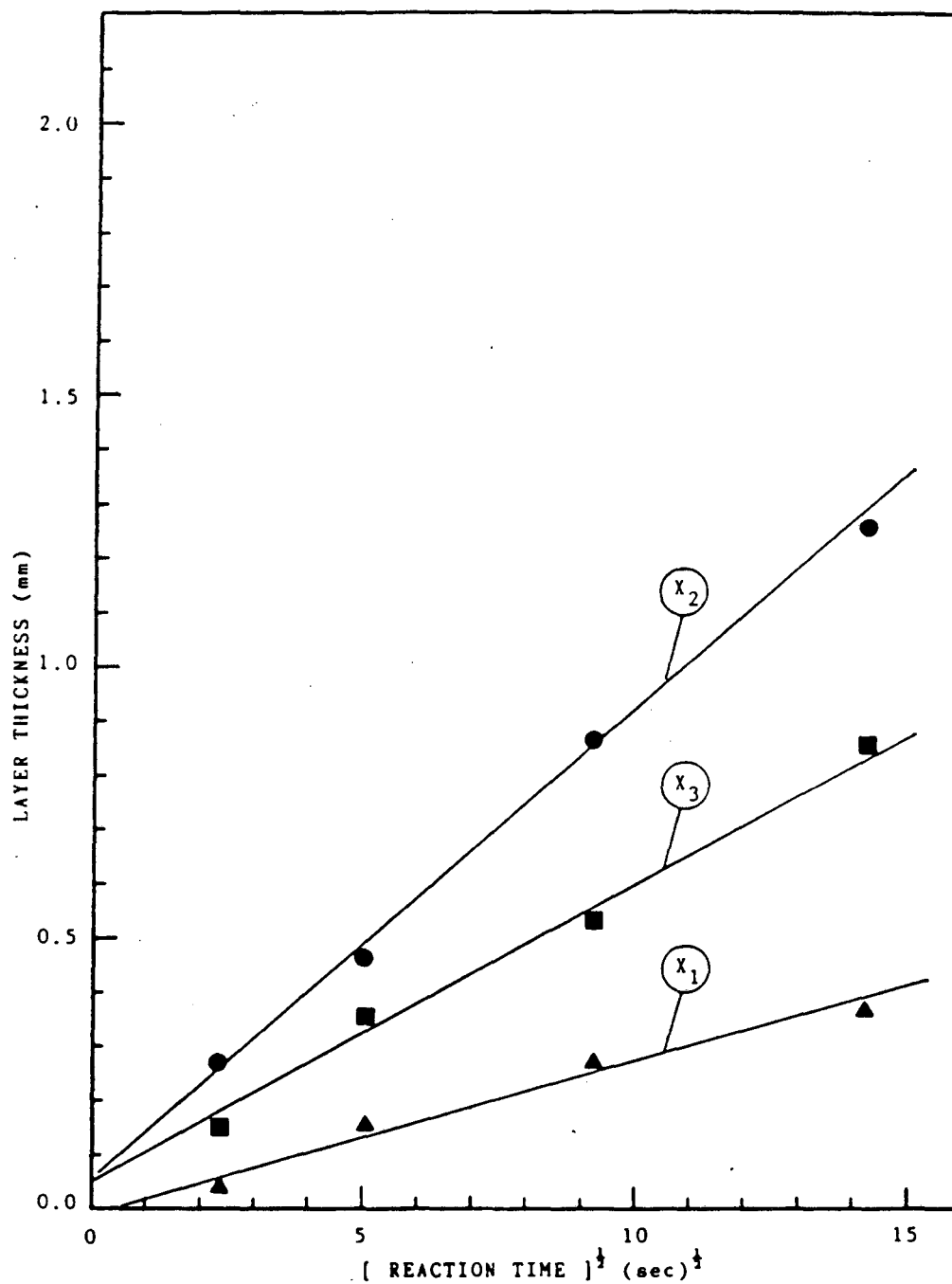


Fig. A.2 UO_2 /Pure Zry Reaction Zone Thickness versus $(\text{Reaction Time})^{1/2}$ at 2000 °C.

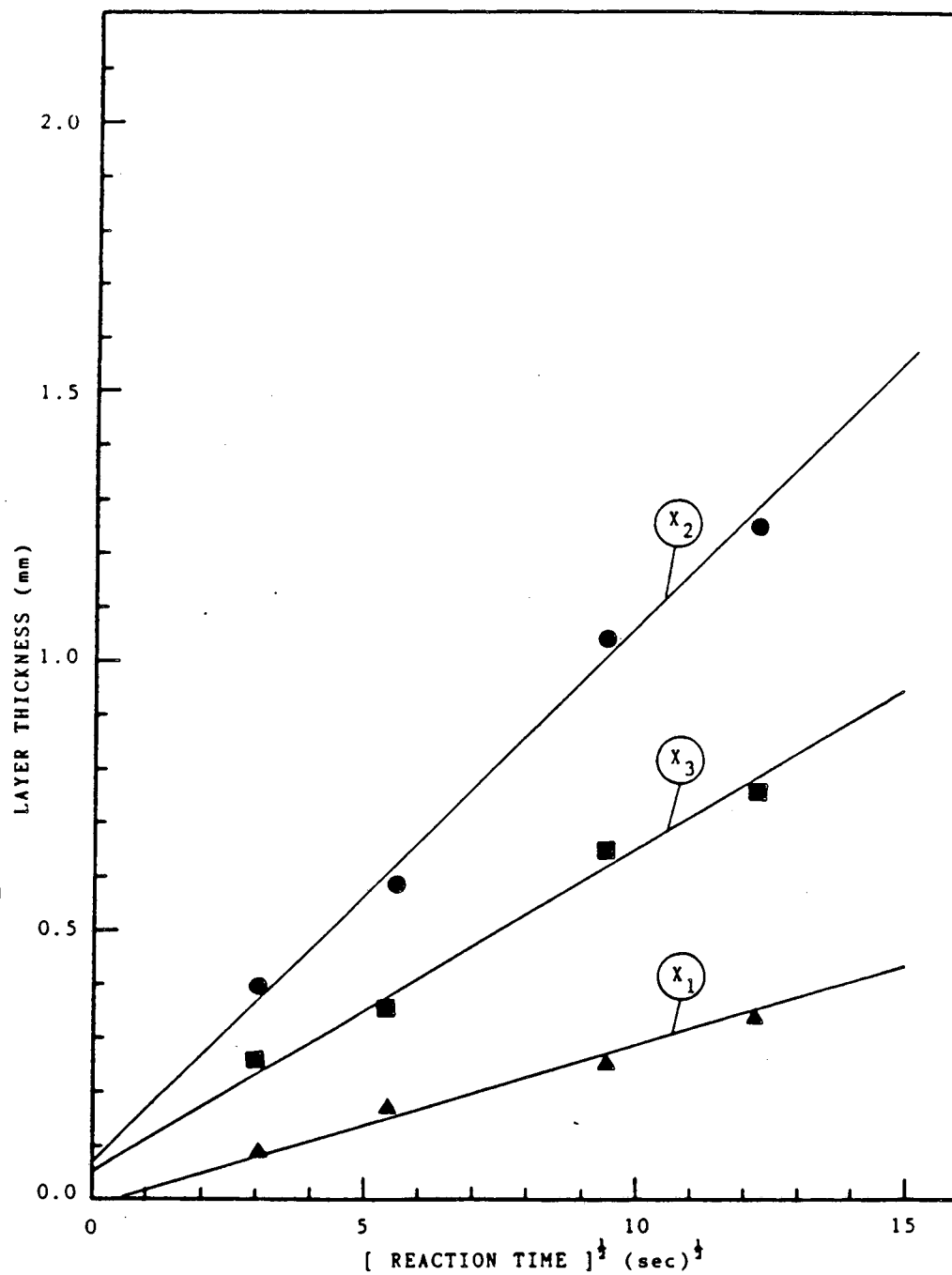


Fig. A.3 UO_2 /Pure Zry Reaction Zone Thickness versus $(\text{Reaction Time})^{1/2}$ at 2100 °C.

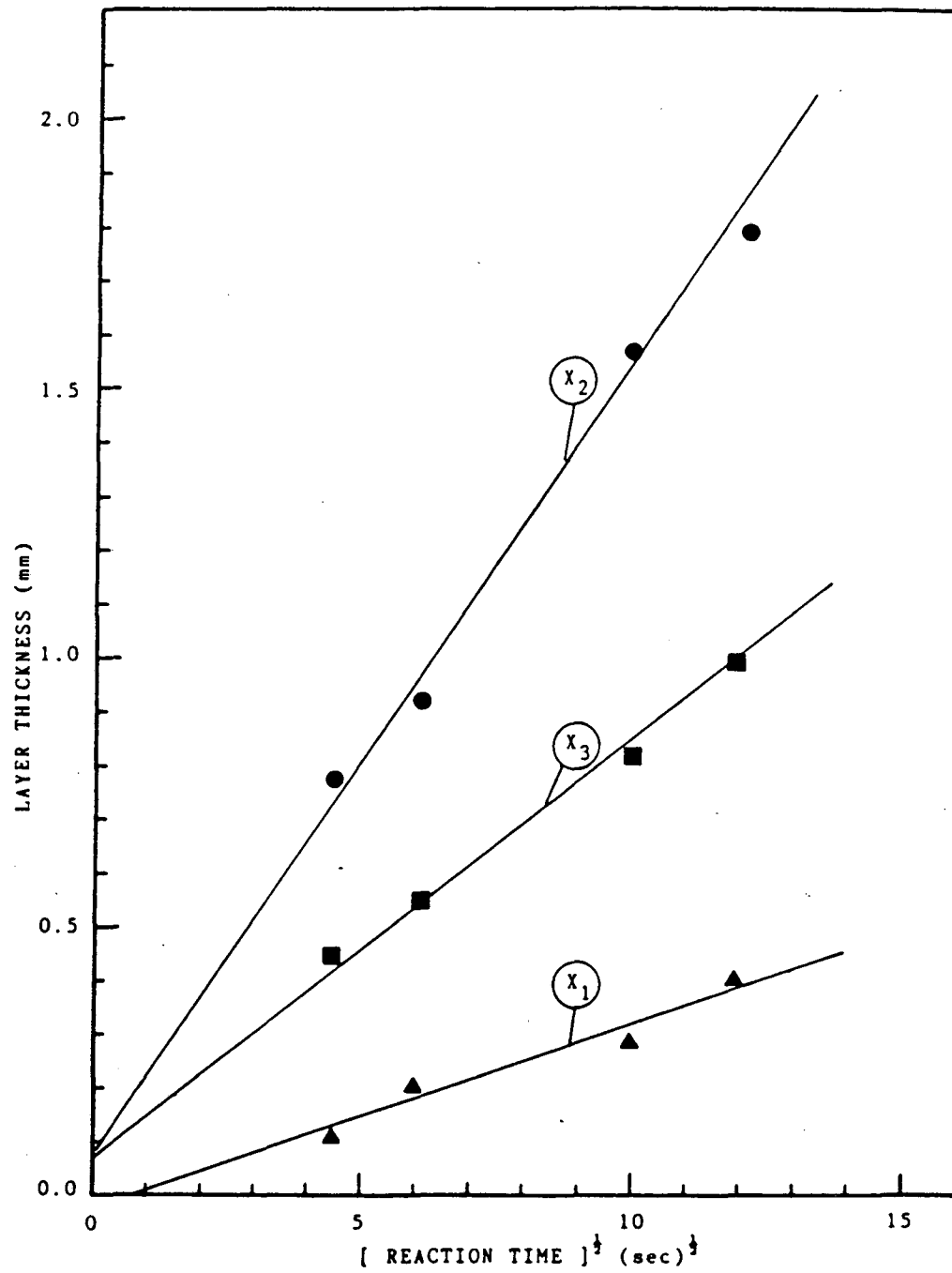


Fig. A.4 UO_2 /Pure Zry Reaction Zone Thickness versus $(\text{Reaction Time})^{1/2}$ at 2200 °C.

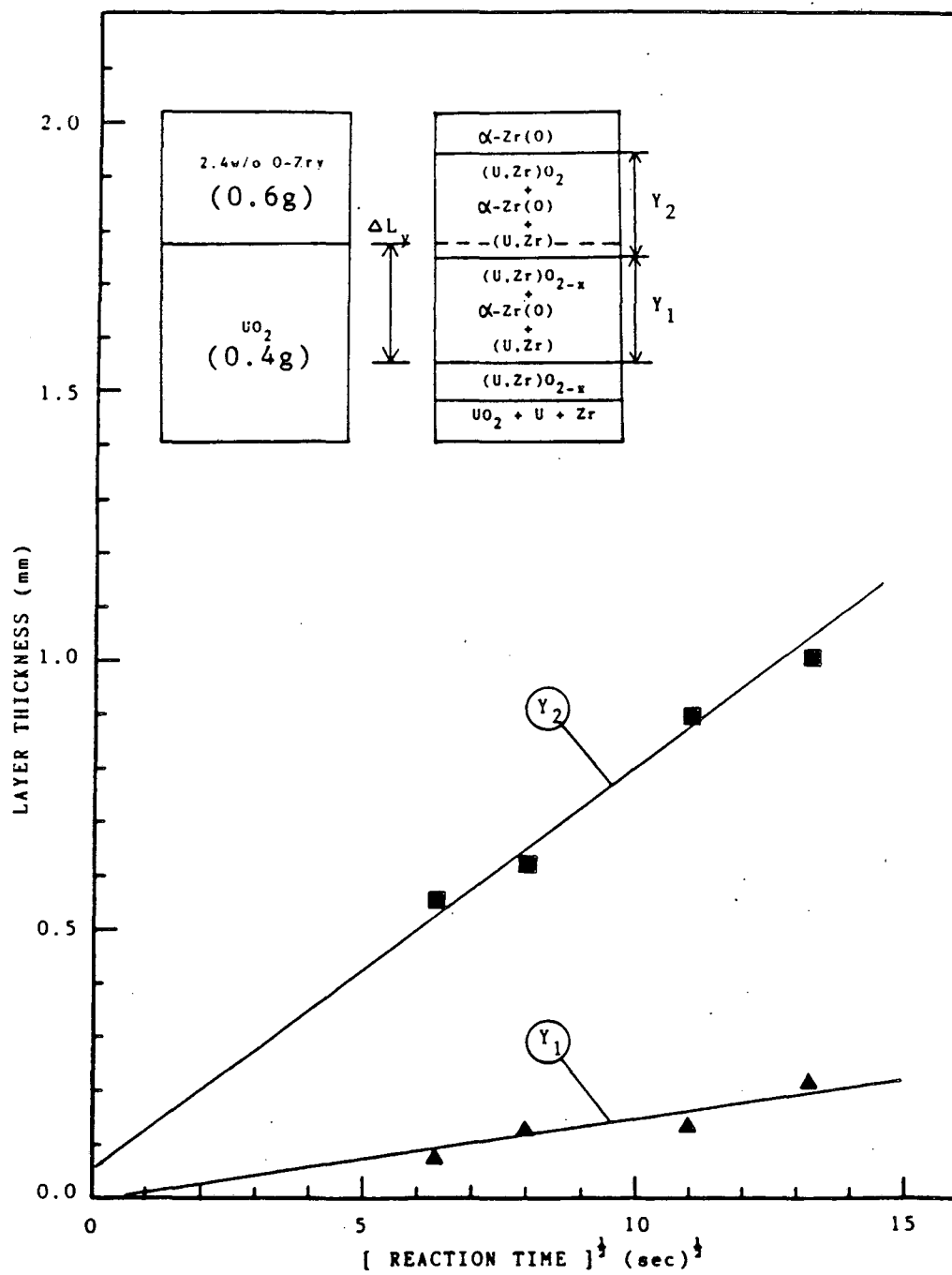


Fig. A.5 $\text{UO}_2/2.4\text{w/o O-Zry}$ Reaction Zone Thickness versus $(\text{Reaction Time})^{1/2}$ at 2000 °C.

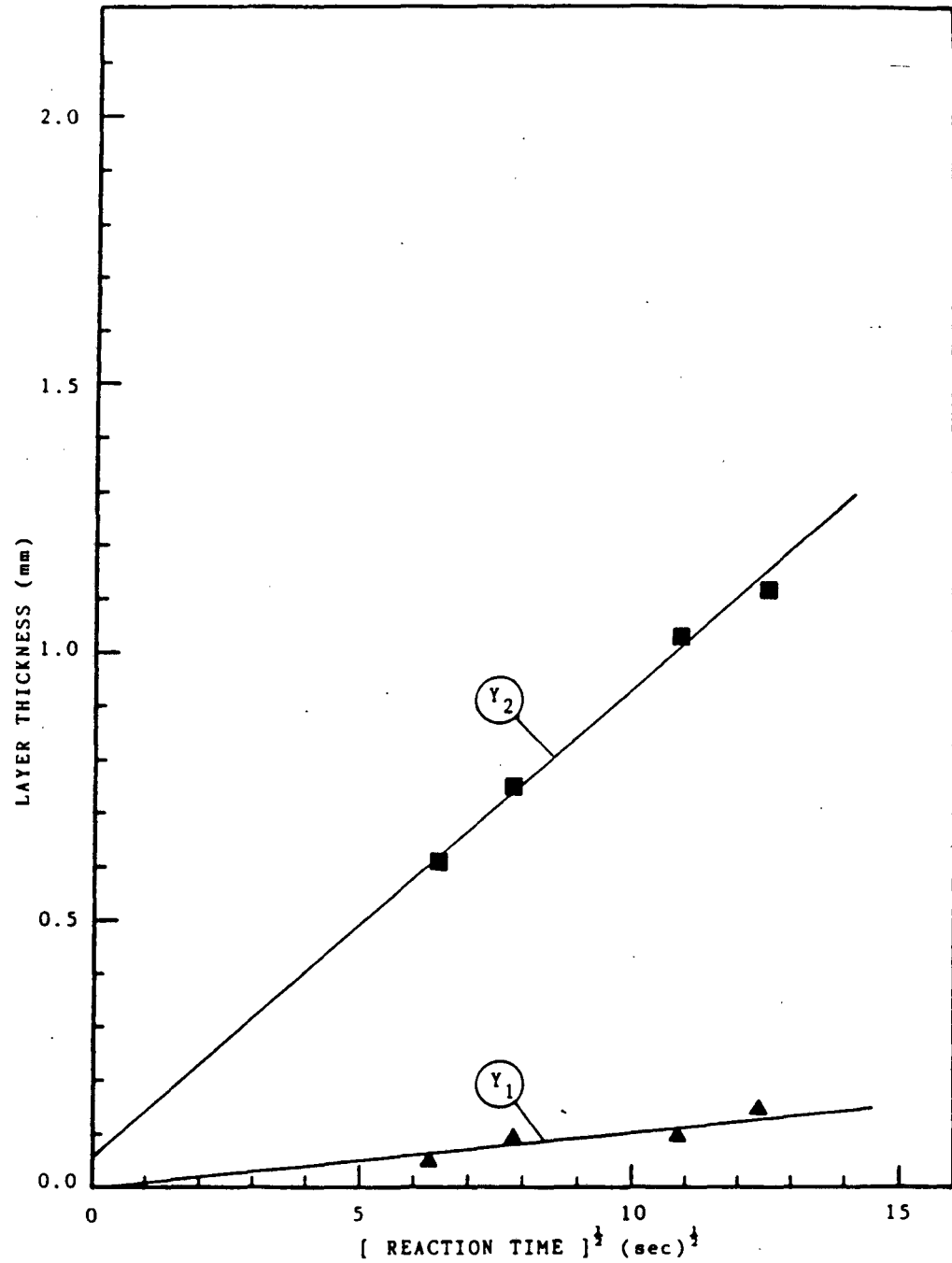


Fig. A.6 $\text{UO}_2/2.4\text{w/o O-Zry}$ Reaction Zone Thickness versus $(\text{Reaction Time})^{1/2}$ at 2100 °C.

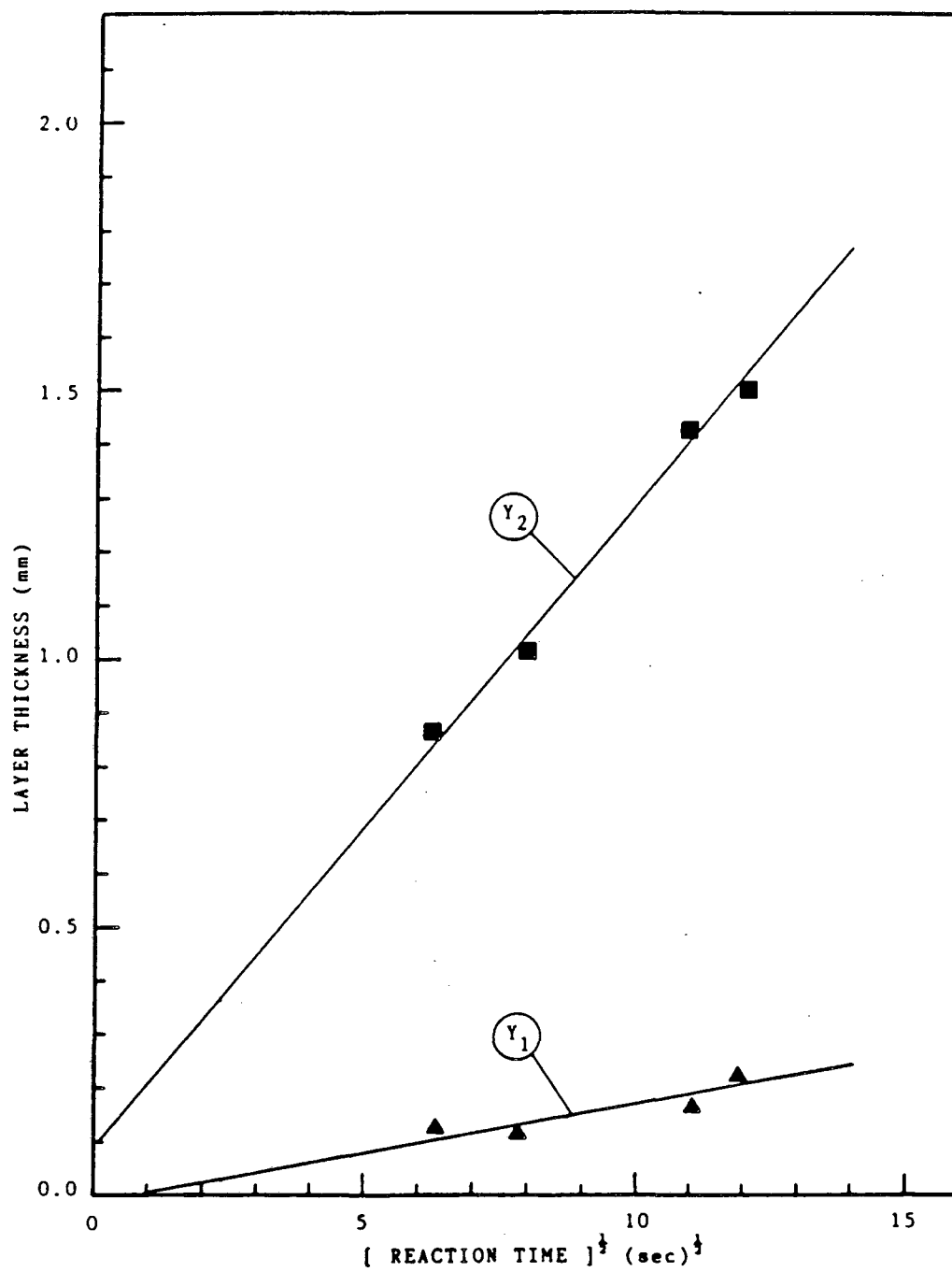


Fig. A.7 $\text{UO}_2/2.4\text{w/o O-Zry}$ Reaction Zone Thickness versus $(\text{Reaction Time})^{1/2}$ at 2200 °C.

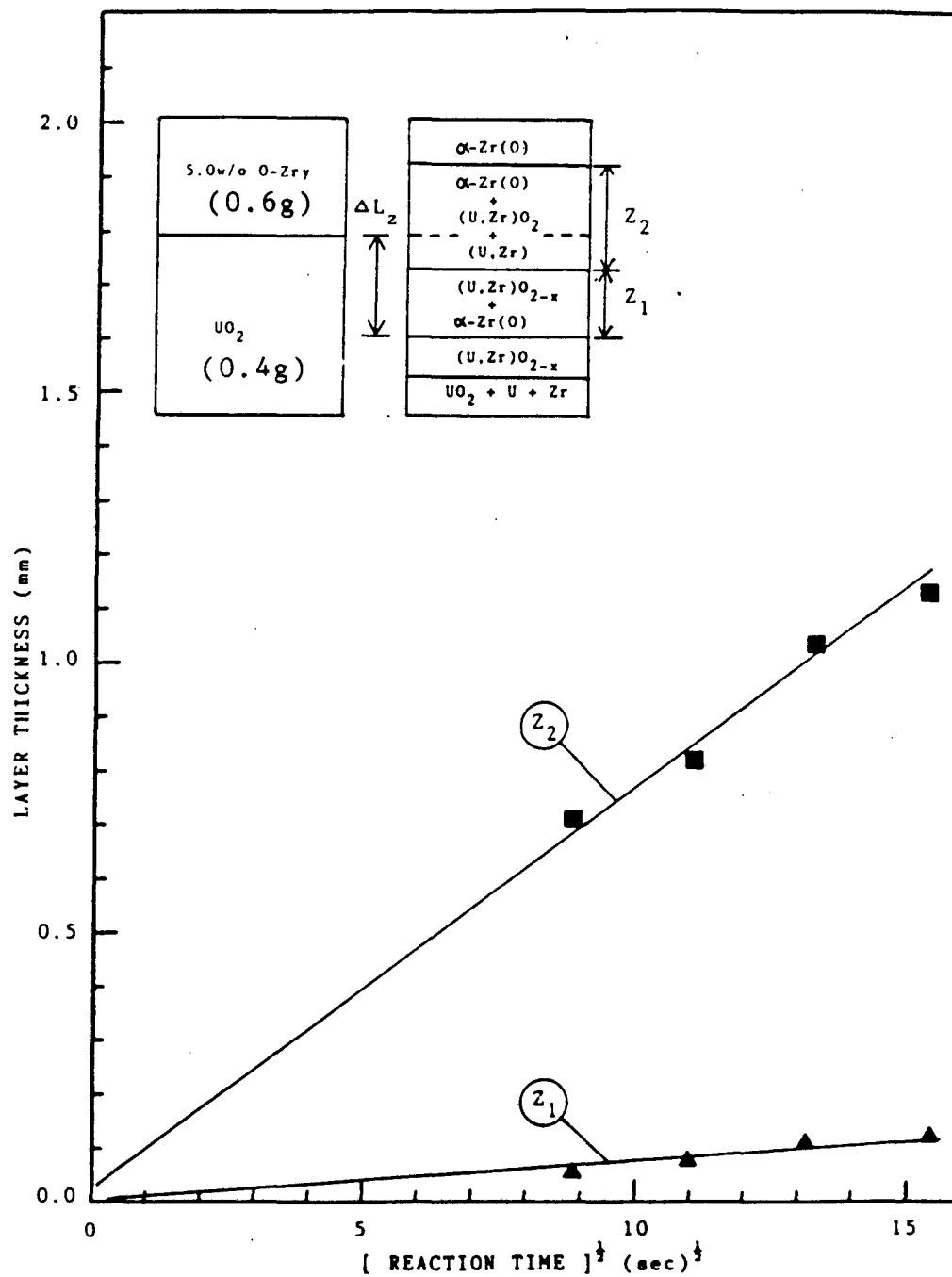


Fig. A.8 $\text{UO}_2/5.0\text{w/o O-Zry}$ Reaction Zone Thickness versus $(\text{Reaction Time})^{1/2}$ at 2000 °C.

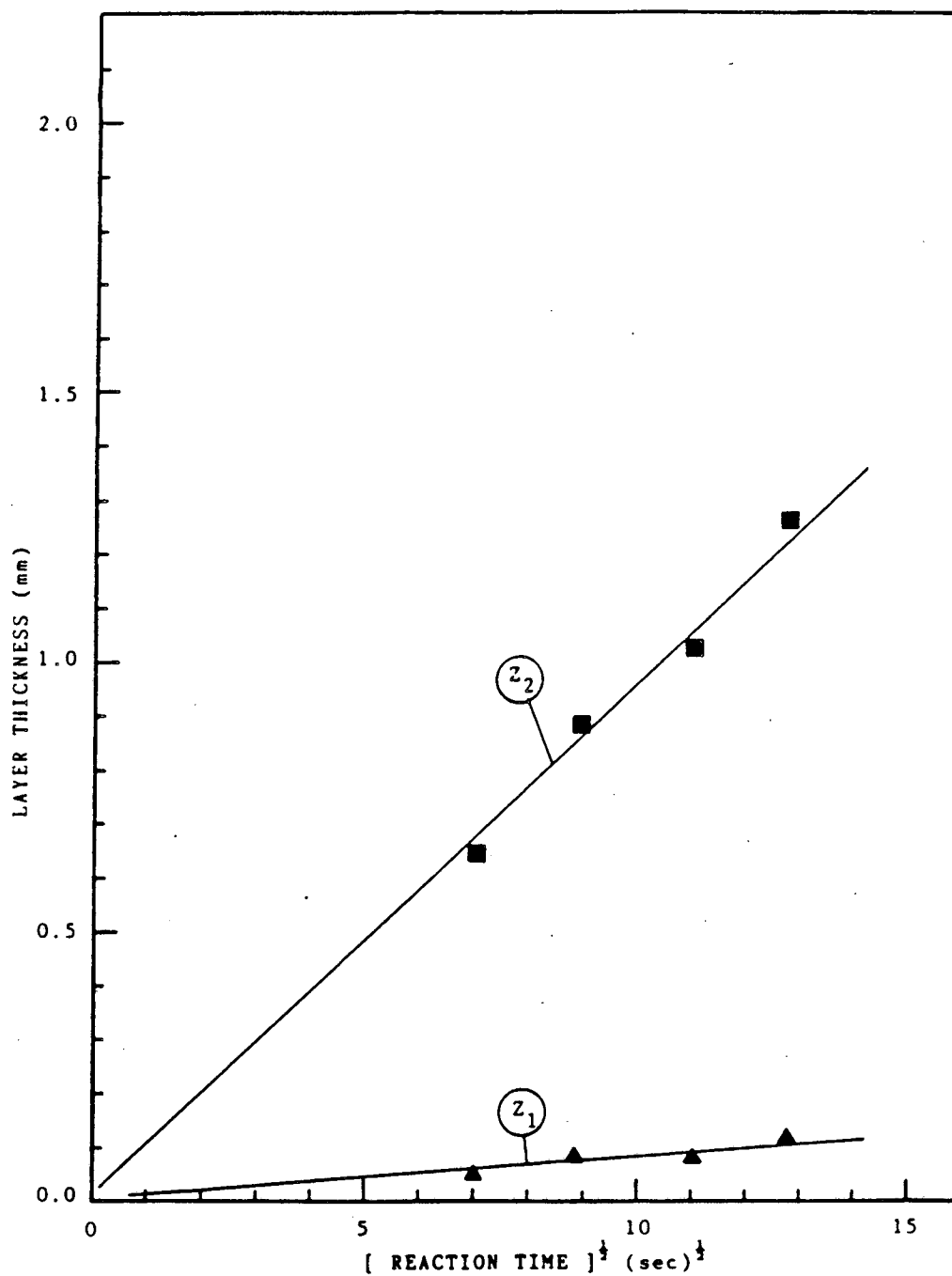


Fig. A.9 $\text{UO}_2/5.0\text{w/o O-Zry}$ Reaction Zone Thickness versus $(\text{Reaction Time})^{1/2}$ at 2100°C .

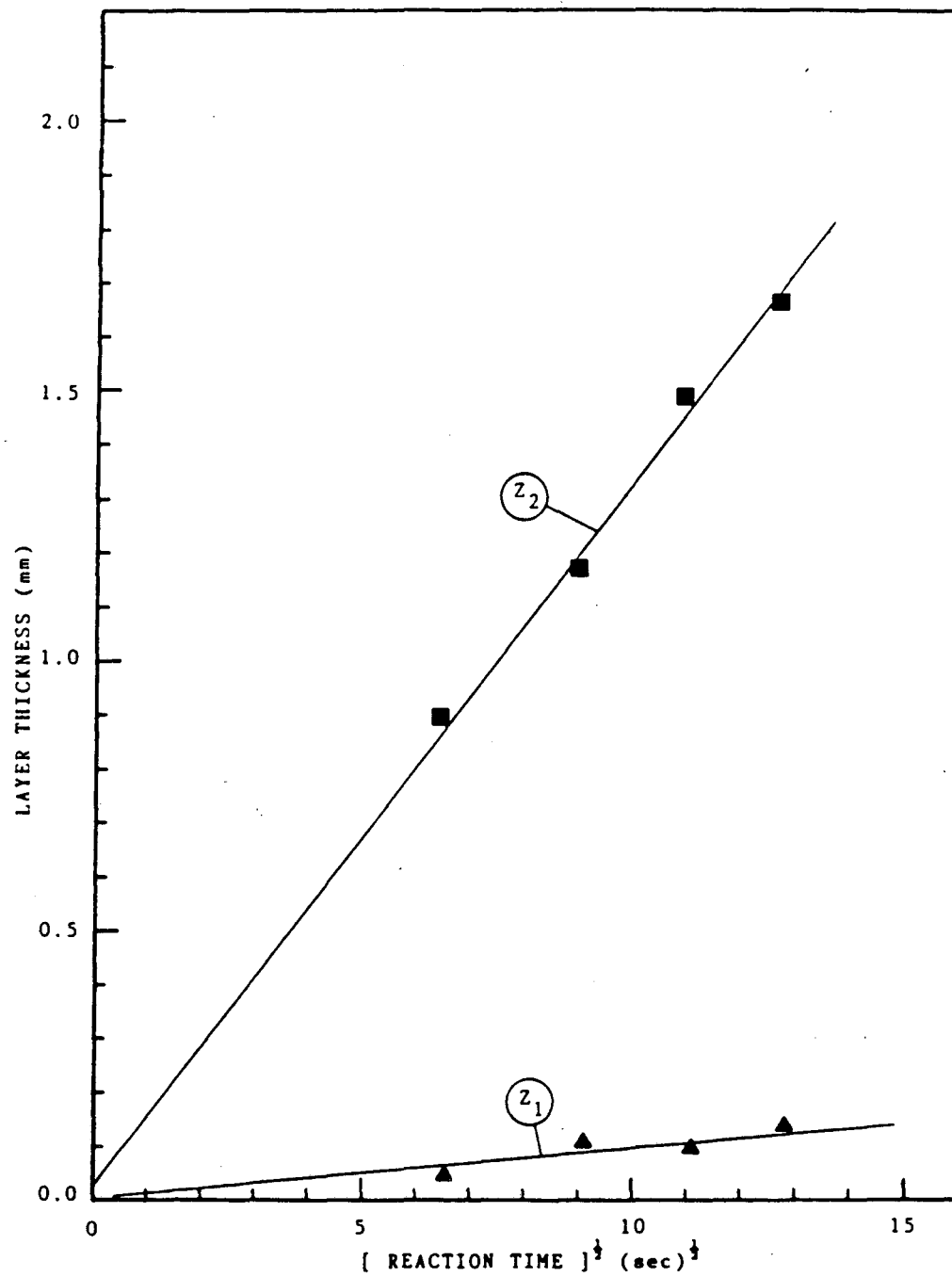


Fig.A.10 $\text{UO}_2/5.0\text{w/o O-Zry}$ Reaction Zone Thickness versus $(\text{Reaction Time})^{1/2}$ at 2200°C .

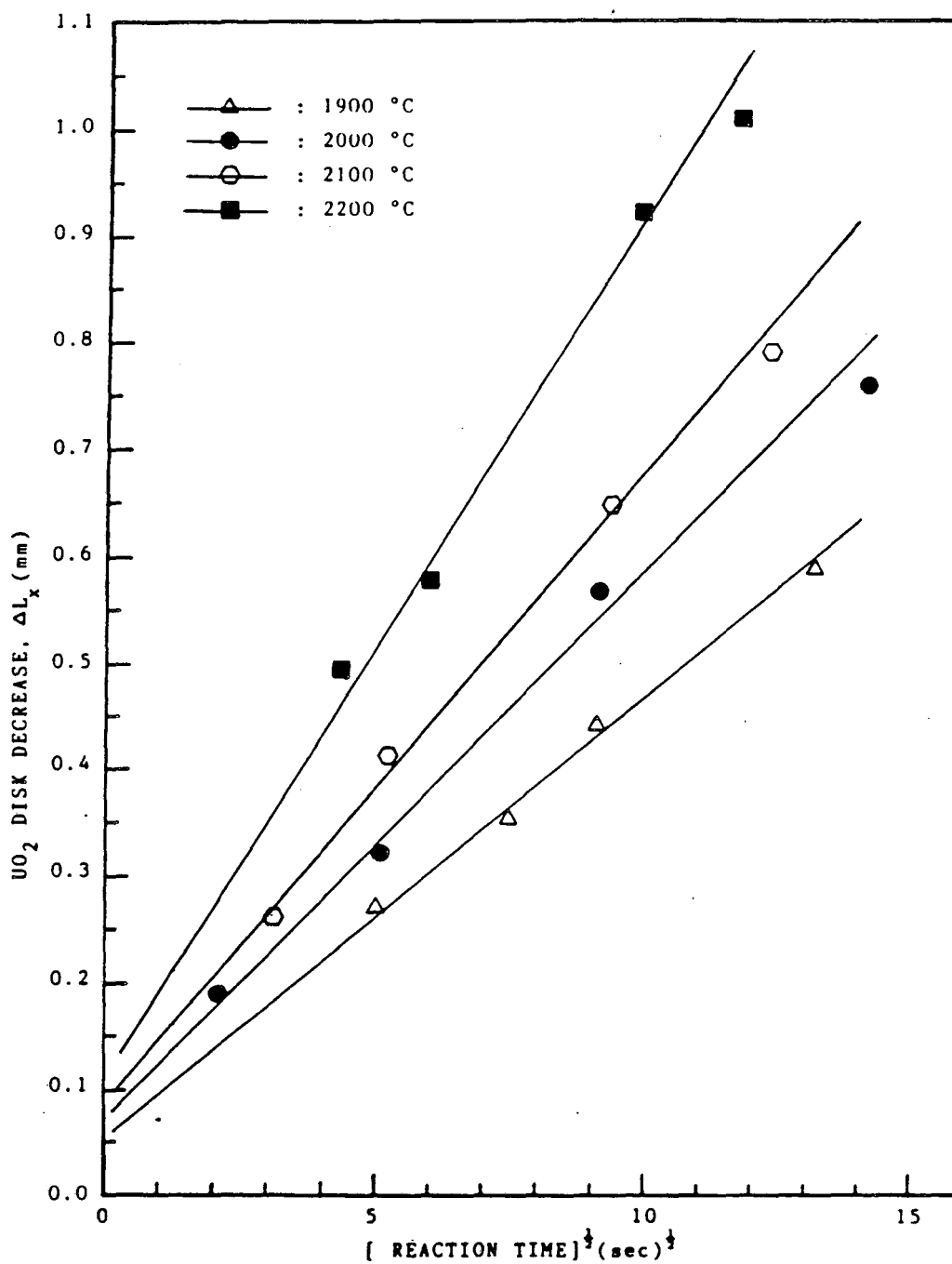


Fig. A.11 UO_2 Disk Thickness Decreases versus (Reaction Time) $^{1/2}$ for UO_2 /Pure Zry System.

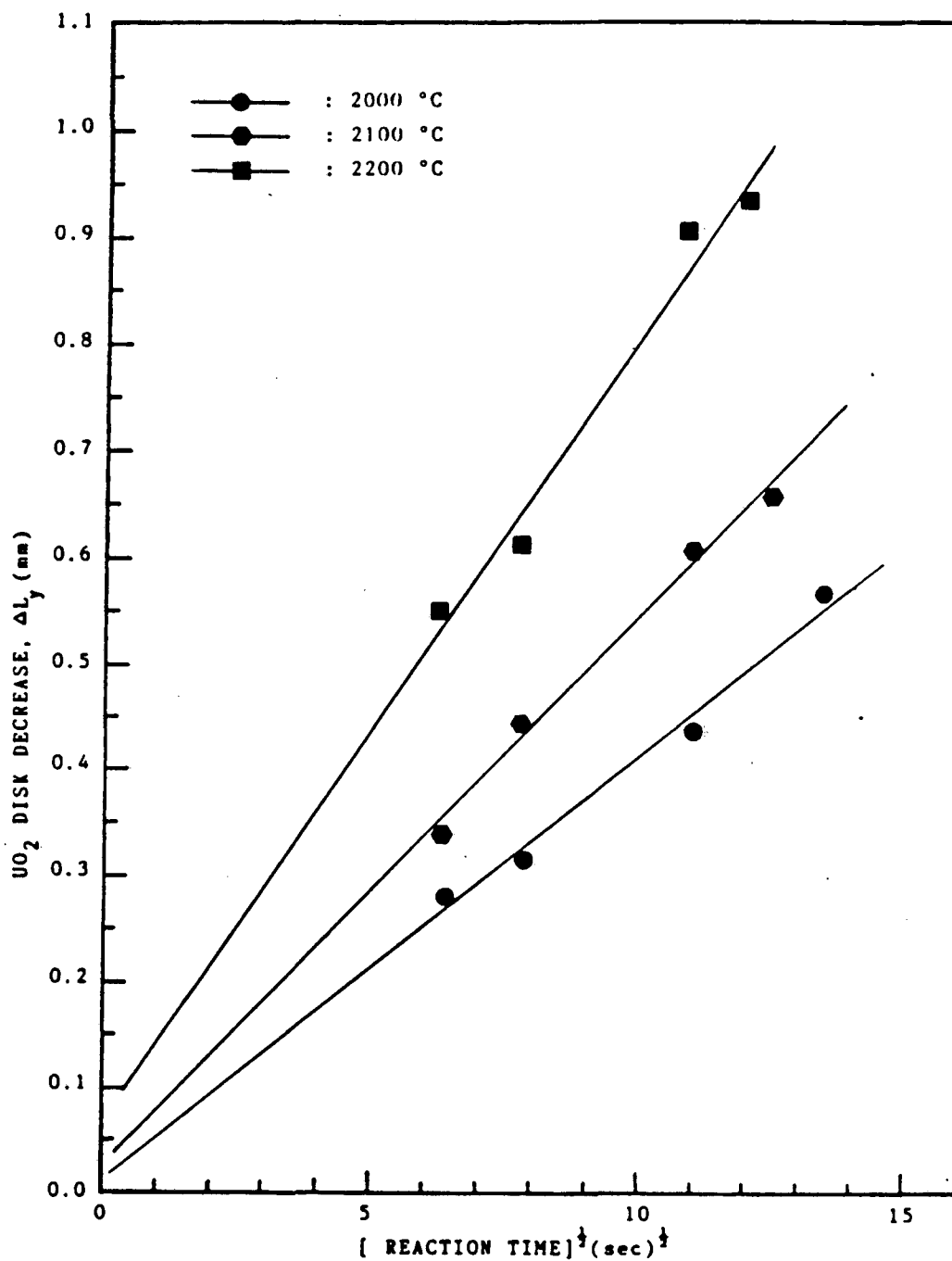


Fig. A.12 UO_2 Disk Thickness Decreases versus (Reaction Time)^{1/2} for $\text{UO}_2/2.4\text{w/o O-Zry}$ System.

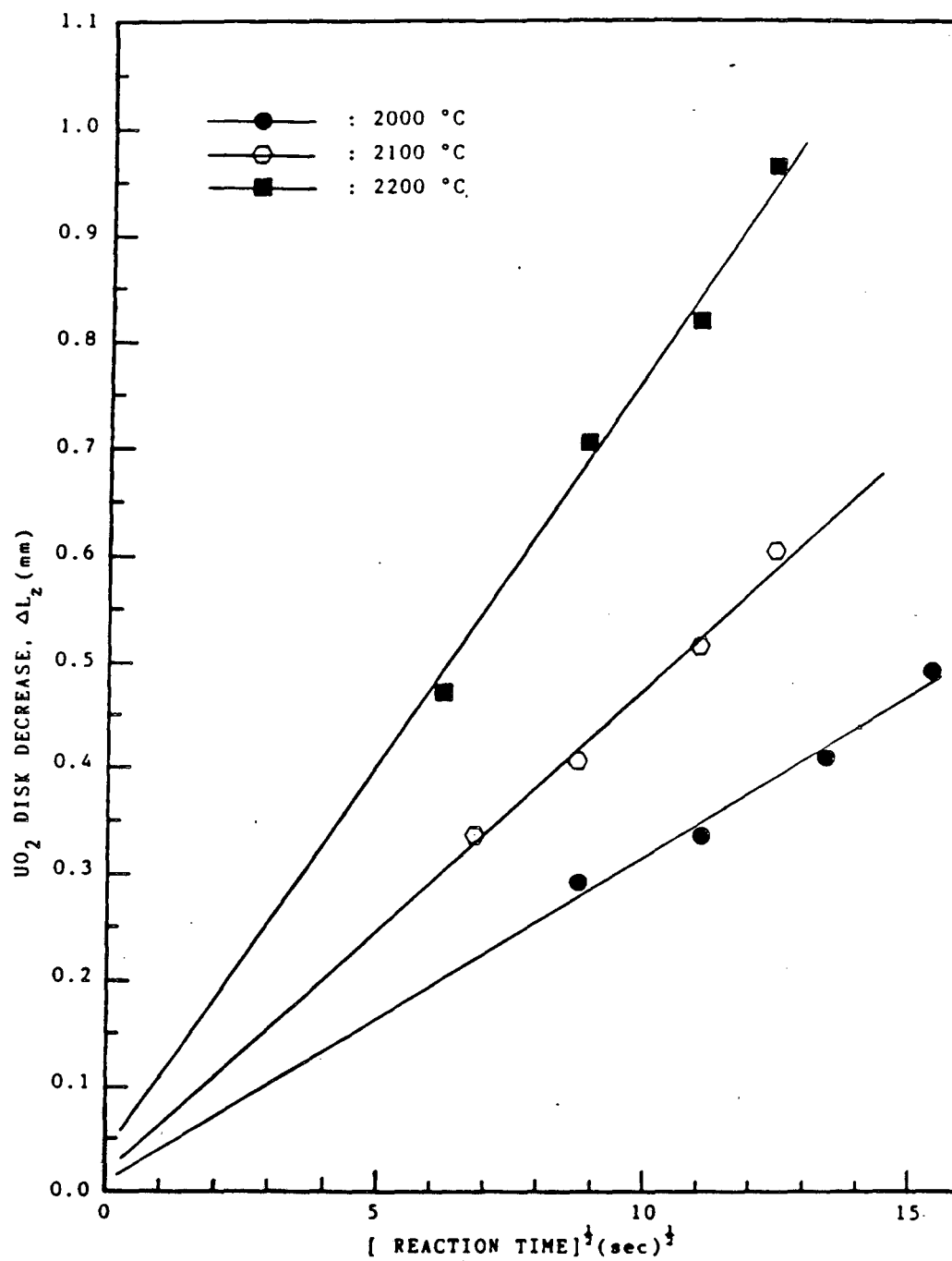


Fig. A.13 UO_2 Disk Thickness Decreases versus (Reaction Time)^{1/2} for $\text{UO}_2/5.0\text{w/o O-Zry}$ System.

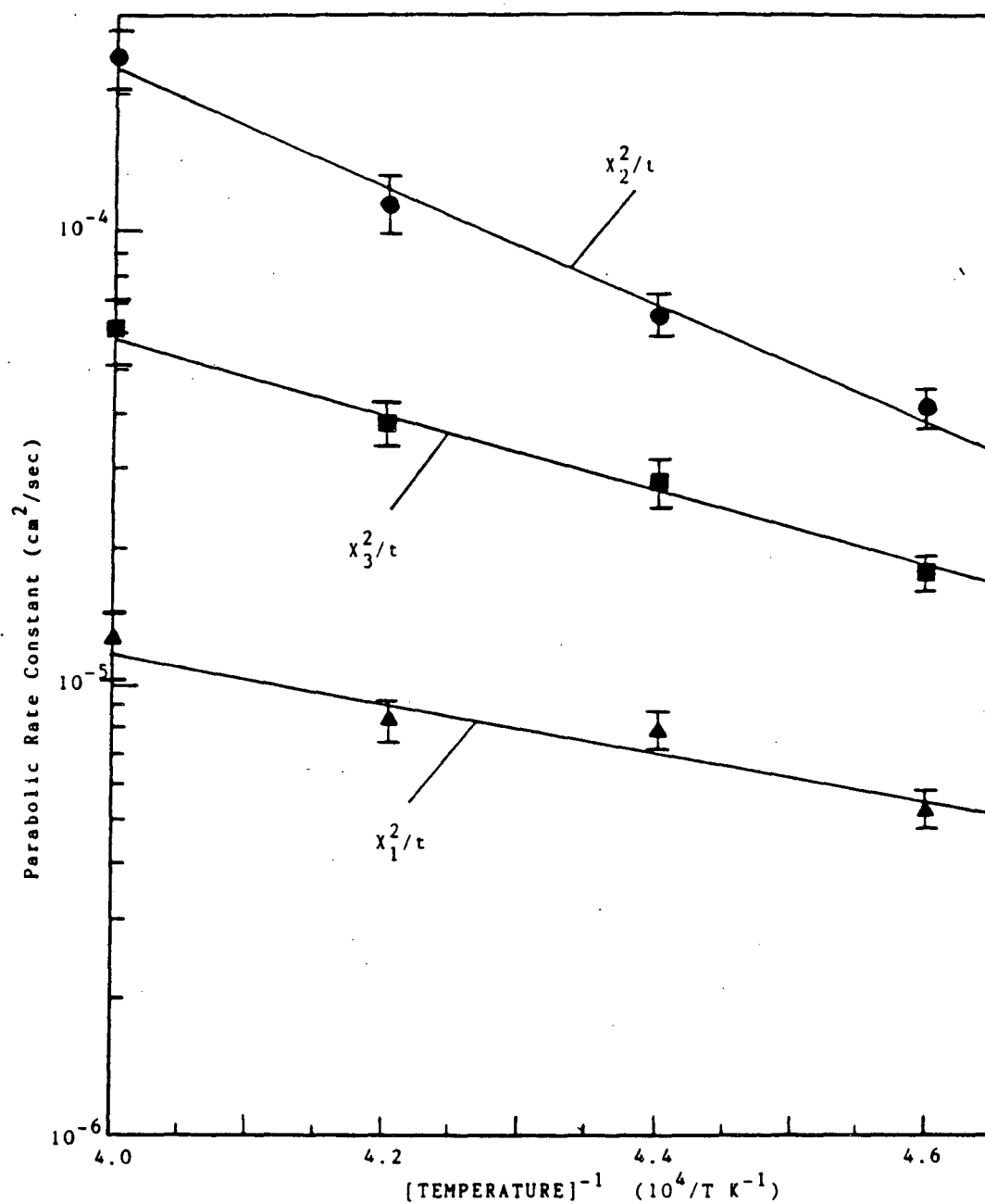


Fig. A.14 UO_2 /Pure Zry Reaction Zone Growth as a Function of Reciprocal Temperature.

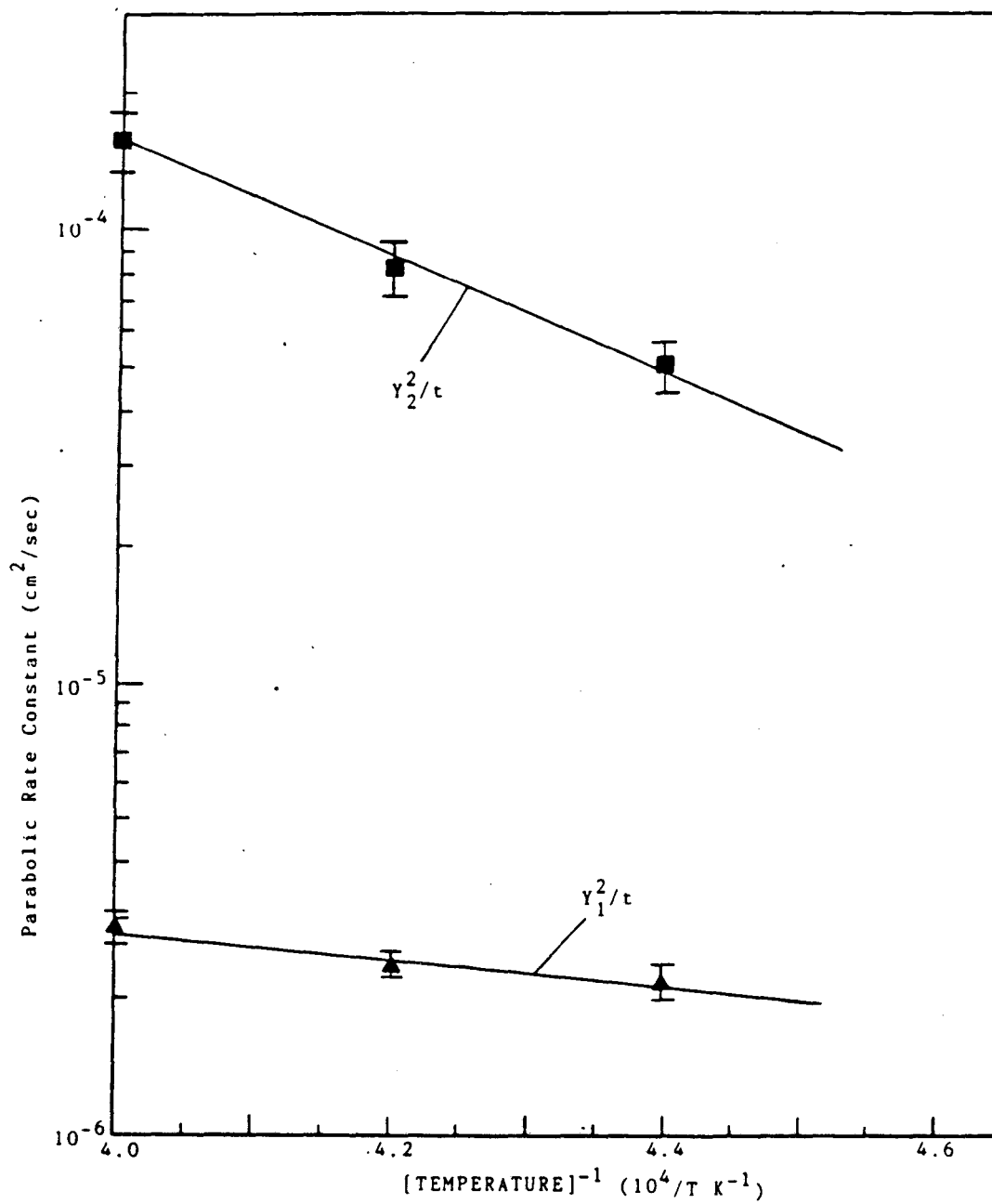


Fig. A.15 $\text{UO}_2/2.4\text{w/o O-Zry}$ Reaction Zone Growth as a Function of Reciprocal Temperature.

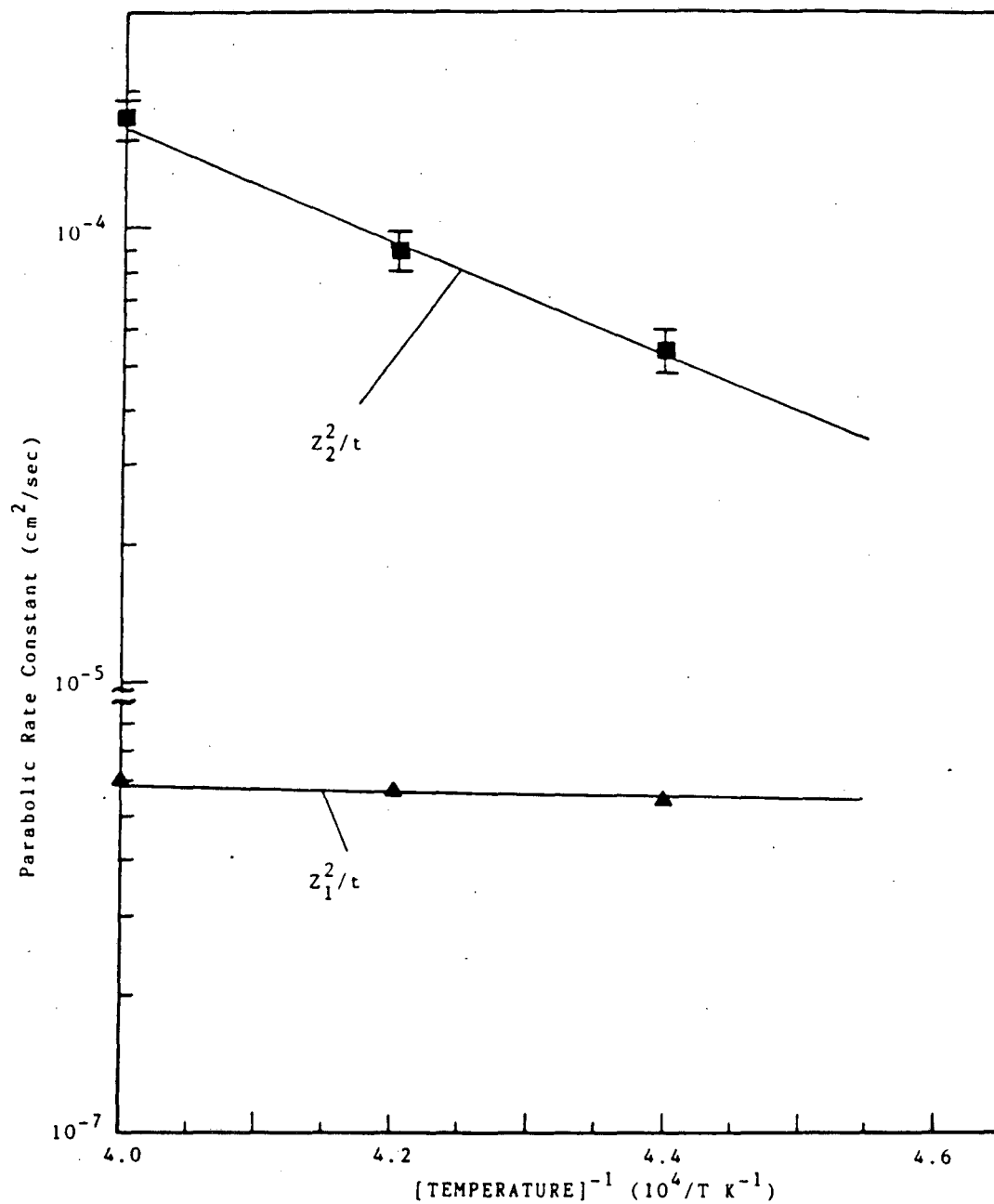


Fig. A.16 UO₂/5.0w/o O-Zry Reaction Zone Growth as a Function of Reciprocal Temperature.

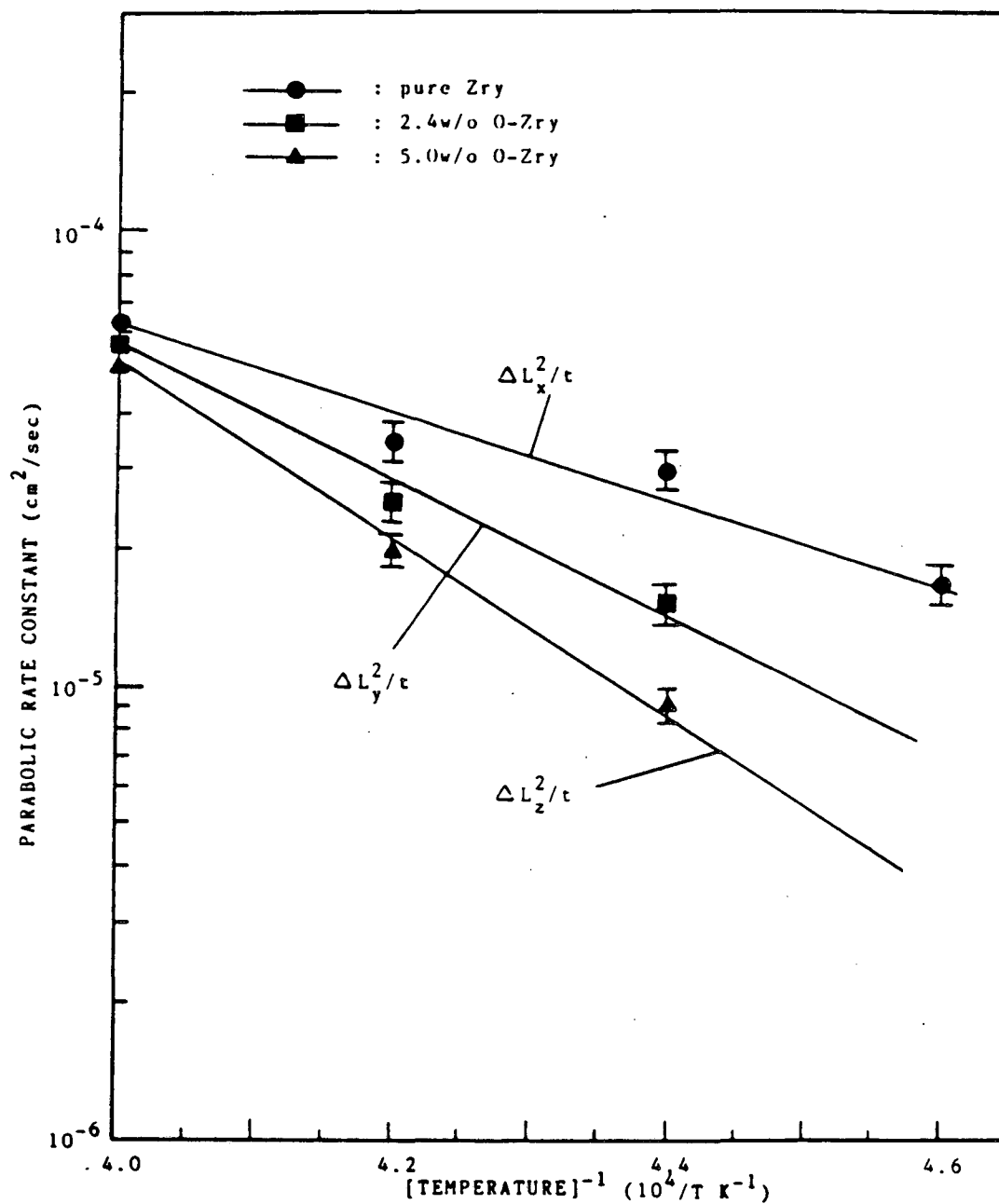


Fig.A.17 Parabolic Rate Constants of UO_2 Disk Thickness Decreases as a Function of Reciprocal Temperature.

APPENDIX B : Calculation of Zirconium Penetration Depth in UO_2

In the UO_2 disk/molten Zry reactions, zirconium particles are found even near bottom of the disk. In order to explain the observed phenomenon, zirconium penetration depth in UO_2 was calculated by using the grain boundary diffusivity of zirconium in UO_{2-x} (D_{gb}). This property is assumed to be $10^6 D_v$, where D_v is the volume diffusivity. Assuming that the x-dependence of D_v^U in UO_{2-x} is the same as that of D_v^{Pu} in $(\text{U}_{0.8}\text{Pu}_{0.2})\text{O}_{2-x}$ (32), we estimate D_v^U in UO_{2-x} as $\sim 100 D_v^U$ in UO_2 . Using D_v^U in UO_2 reported by Reimann & Lundy (33), we obtain D_v^U in $\text{UO}_{2-x} = 6 \times 10^{-12} \text{ cm}^2/\text{s}$ at 2100°C , and thus $D_{gb} = 6 \times 10^{-6} \text{ cm}^2/\text{s}$. The penetration depth (z) = $\sqrt{Dt}$, for which we obtain $z \leq 0.33 \text{ mm}$ for 180 s. This penetration depth is an order of magnitude smaller than the thickness of the UO_2 disk (2.2 mm).

APPENDIX C : Calculation of the Kinetics of Dissolution of the UO_2 Disk by One-Dimensional Diffusion in a Semi-Infinite Medium

In order to model dissolution of the UO_2 disk, the dissolution rate was calculated using one-dimensional diffusion equation and assuming constant liquid density :

$$\frac{\partial C_u}{\partial t} = D \frac{\partial^2 C_u}{\partial z^2} \quad (\text{C.1})$$

where C_u is the mass fraction of uranium in the melt (on an oxygen-free basis) at depth z from the melt/solid interface and D is the diffusion coefficient of uranium in liquid Zry.

If the boundary and initial conditions for a semi-infinite system are

$$\begin{aligned} C &= 0 & \text{at } t &= 0, \\ C &= C_{su} & \text{at } z &= 0, \\ C &= 0 & \text{at } z &= \infty, \end{aligned}$$

the solution is

$$\frac{C_u}{C_{su}} = \text{erfc} \left(\frac{z}{2\sqrt{Dt}} \right) \quad (\text{C.2})$$

where erfc is the complementary error function

A reasonable criterion for the applicability of Eq (C.2) to the UO_2 /molten Zry system is that the concentration rise at the top surface of the molten Zry should be less than, say, 0.5 % of that imposed at the bottom of the molten Zry (i.e., the UO_2 /molten Zry interface). This occurs when the argument of the complementary error function is ~ 2 . Consequently, the maximum time at which the solution is applicable is $t_{\max} = \frac{H^2}{16D}$, in which H = the height of the molten Zry (0.5cm). If $t \leq t_{\max}$, the following expression for the fractional approach to saturation is obtained :

$$\frac{M_t}{M_\infty} = \frac{1}{H} \int_0^H \frac{C_u}{C_{su}} dz = 2 \left[\frac{Dt}{\pi H^2} \right]^{1/2} \quad (C.3)$$

where M_t = the quantity of uranium which has entered the molten Zry in time t and M_∞ = the corresponding quantity after infinite time.

The mutual diffusion coefficient of the U-Zr liquid metal alloy was estimated as follows. The diffusivity of lanthanum in liquid uranium was measured at 1250 °C to be 1.5×10^{-5} cm²/s(43). This value was assumed to be applied to the U-Zr system and extrapolated to 2000 °C by assuming that activation energy for liquid diffusion is equal to that for uranium viscosity, the latter being 6.5 kcal/mole(44). The best estimate of D is 3.0×10^{-5} cm²/s at 2000 °C. Using this value of D and $H=0.5$ cm, equation (C.3) is plotted as the curve in Fig. 4.15. Note that $t_{\max}$ for the present test is ~ 500 s.

In order to normalize the experimental data at 2000 °C(Fig. A.11), the maximum decrease of the UO₂ disk thickness(ΔL_∞) is needed. This value can be calculated as follows. From Eq. (G.5), the saturation mass fraction of uranium(C_{su}) at 2000 °C is 0.41. However, the total quantity of uranium dissolved at saturation is

$$M_\infty = \pi R_d^2 H C_{su} \rho_m \quad (C.4)$$

where $R_d=0.25$ cm is the radius of the UO₂ disk and ρ_m is the total density of the metal, estimated to be ~ 8 g/cm³[Eq. (D.4)]. Using $C_{su}=0.41$ and $H=0.5$ cm in Eq. (C.4), M_∞ is calculated as 0.32 g. Using the area of the disk wetted by the melt and the density of UO₂(10.96 g/cm³), M_∞ is converted to yield the maximum decrease of the UO₂ disk thickness(ΔL_∞) of 0.19 cm. This value is used in normalizing the experimental disk thickness decrease data to give the ordinate points in Fig. 4.15.

APPENDIX D : Dissolution Kinetics of the UO_2 Crucible

The rate of uranium dissolution in the UO_2 crucible/molten Zry reactions is quite large during the incubation period. In order to model this phenomenon, the fractional increase of uranium concentration in the melt was calculated as a function of time for two limiting cases : a) uranium transport by natural convection and b) uranium transport by two-dimensional diffusion in molten Zry.

D.1 Uranium Transport by Natural Convection

Uranium transport by natural convection can be described by the following expression :

$$J = k \rho_m (C_{su} - C_{bu}) \quad (\text{D.1})$$

in which J = flux of uranium into the molten Zry, k = mass-transfer coefficient, ρ_m = average liquid density, C_{su} = mass fraction of uranium in the molten Zry contacting the UO_2 crucible, and C_{bu} = mass fraction of uranium in the bulk molten Zry. The mass fraction of uranium is on an oxygen-free basis. A schematic diagram of the uranium concentration distribution is shown in Fig. D.1. The mass-transfer coefficient(k) for laminar natural convection flow can be estimated by the following equations described in section 1.3 :

$$Ra = \left[\frac{\Delta \rho}{\rho_m} \right] \left[\frac{gd^3}{\nu^2} \right] \left[\frac{\nu}{D} \right] \quad (\text{D.2})$$

$$Nu = \frac{kd}{D} = B Ra^{\frac{1}{4}} \quad (\text{D.3})$$

in which $\Delta \rho = \rho_s - \rho_b$ = density difference between the liquid contacting the UO_2 crucible(i.e., liquid having a mass fraction of C_{su}) and the liquid in the bulk region with uranium mass fraction C_{bu} , and $\rho_m = \frac{\rho_s + \rho_b}{2}$ = mean density. In addition, d = diameter of the UO_2 crucible, ν = viscosity of the molten Zry, D = mutual diffusion coefficient of the U-Zr metal alloy, g is the acceleration of gravity, $B = 0.54$ for an enclosure, and $B = 0.57$ for a vertical

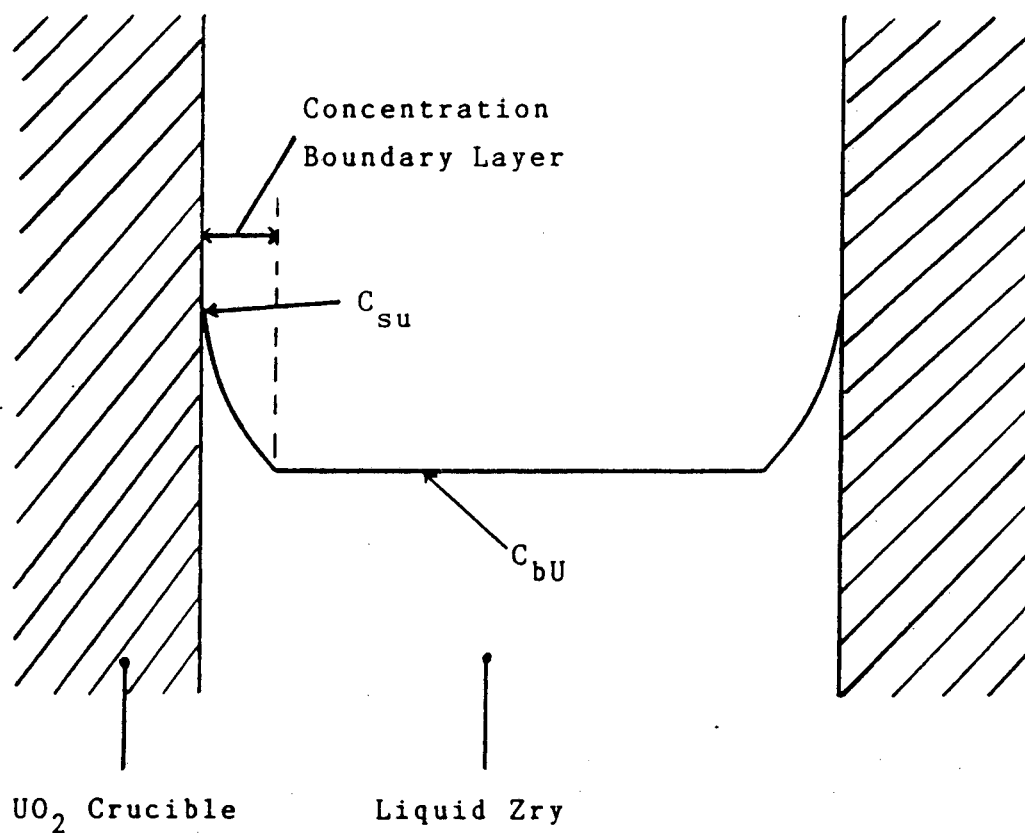


Fig.D.1 Schematic Diagram of the Radial Concentration Distribution of Uranium in Molten Zry during Natural Convection-dominated Transport.

plate.

Assuming ideal mixing of U and Zr(on an oxygen-free basis), ρ is calculated as :

$$\rho = \left[\frac{C_{su}}{\rho_u} + \frac{1-C_{su}}{\rho_{Zr}} \right]^{-1} \quad (D.4)$$

in which $\rho_u = 17.0 \text{ g/cm}^3$ and $\rho_{Zr} = 5.8 \text{ g/cm}^3$.

Here, it is assumed that C_{su} is the saturation mass fraction of uranium of the molten Zry, as discussed in Appendix G. From Eq. (G.5), C_{su} at 2200°C is 0.78. Using this value in Eq. (D.4), we obtain $\rho_m(0)=8.6\text{g/cm}^3$. Then, by linearizing Eq. (D.4) and assuming $\rho_m(t)=\rho_m(0)=8.6\text{g/cm}^3$, $\frac{\Delta\rho(t)}{\rho_m(t)}$ for $t>0$ is approximated as :

$$\frac{\Delta\rho(t)}{\rho_m(t)} = \alpha(C_{su} - C_{bu}) \quad (D.5)$$

in which $\alpha = \frac{1}{\rho_m(0)} \frac{\rho_{Zr}\rho_u}{\rho_u - \rho_{Zr}} = 1.0$.

Using Eq. (D.5) in (D.2), Ra is calculated as :

$$Ra = \beta(C_{su} - C_{bu}) \quad (D.6)$$

in which $\beta = \frac{\alpha g d^3}{\nu D}$.

Then, Eq. (D.3) is used to obtain the Nusselt number for the present system because the calculated Ra indicates that the flow is in laminar regime :

$$Nu = \gamma(C_{su} - C_{bu})^{\frac{1}{4}} \quad (D.7)$$

in which $\gamma = B\beta^{\frac{1}{4}}$.

Since $Nu = \frac{k d}{D}$, rearrangement gives

$$k = \delta(C_{su} - C_{bu})^{\frac{1}{4}} \quad (D.8)$$

$$\delta = \frac{\gamma D}{d} = B \left[\frac{\alpha g d^3}{\nu D} \right]^{\frac{1}{4}} \left[\frac{D}{d} \right] \quad (\text{D.9})$$

The uranium balance on the melt is :

$$V \rho_m \frac{dC_{bu}}{dt} = SJ \quad (\text{D.10})$$

in which V = volume of the molten Zry and S = surface area of the UO₂ crucible in contact with the molten Zry.

Substitution of Eqs. (D.1) and (D.8) in Eq. (D.10) yields :

$$V \frac{dC_{bu}}{dt} = Sk(C_{su} - C_{bu}) = \delta S(C_{su} - C_{bu})^{\frac{5}{4}} \quad (\text{D.11})$$

Equation (D.11) can be integrated to give

$$\frac{C_{bu}}{C_{su}} = 1 - \left(\frac{\delta S}{4V} t + 1 \right)^{-4} \quad (\text{D.12})$$

Equation (D.12) indicates that $\frac{C_{bu}}{C_{su}}$ depends strongly on $\frac{S}{V}$. Note that δ is not a function of $\frac{S}{V}$. By using Eq. (D.9), δ in Eq. (D.12) is calculated as follows. Viscosity of the U-Zr liquid is assumed to be that of molten Zry (0.0138 cm²/s). The diameter of the UO₂ crucible is 0.5 cm and B is 0.54. Substituting these values into Eq. (D.9) and $g = 980 \text{ cm/s}^2$ yields $\delta = 4.6 \times 10^{-3} \text{ cm/s}$. By using this value, equation (D.12) is plotted in Fig. D.2 to show the dependence of $\frac{C_{bu}}{C_{su}}$ on $\frac{S}{V}$. This figure shows that the larger value of $\frac{S}{V}$ gives the more rapid approach to saturation. For the UO₂ crucible/molten Zry geometry, $\frac{S}{V}$ is ~ 15 . Using the values of δ and $\frac{S}{V}$ given above, equation (D.12) is plotted as the upper curve in Fig. 4.16.

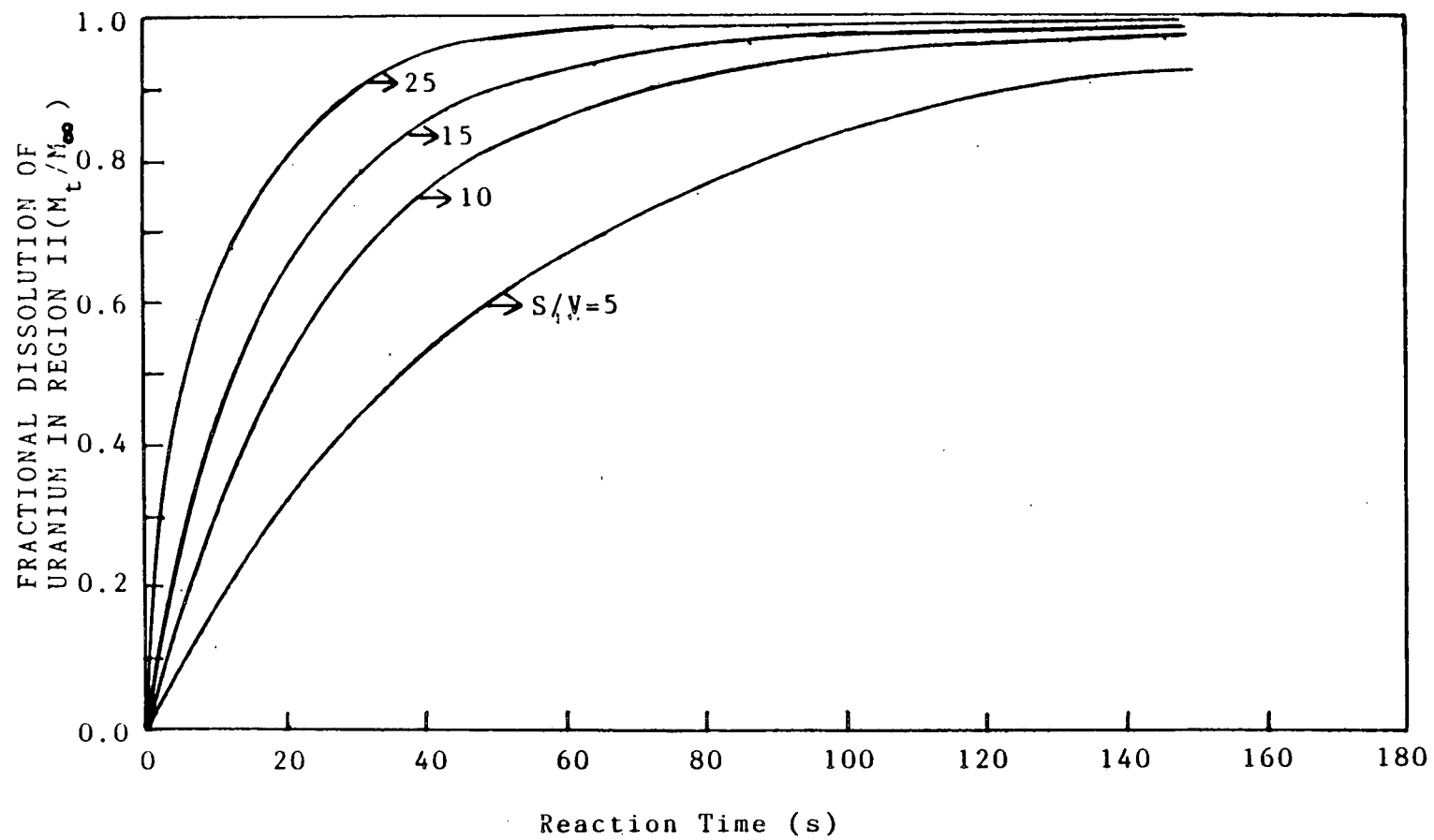


Fig. D.2 Dependence of Fractional Dissolution of Uranium in the Melt on S/V for the UO_2 Crucible/Pure Zry Reactions at 2200°C .

D.2 Uranium Transport by Two-Dimensional Diffusion in the Molten Zry

The two-dimensional form of Fick's law is :

$$\frac{\partial C_u}{\partial t} = D \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_u}{\partial r} \right) + \frac{\partial^2 C_u}{\partial z^2} \right] \quad (D.13)$$

In the UO_2 crucible/molten Zry system, the top surface of the molten Zry was not contacted by the UO_2 crucible. For this system, the boundary and initial conditions are :

$$C_u = C_{su}, \text{ on the cylindrical surface at all times and the bottom,}$$

$$\frac{\partial C_u}{\partial z} = 0, \quad \text{at the top surface at all times,}$$

$$C_u = 0, \quad \text{in the bulk at } t = 0$$

With the free surface at the top, the diffusion problem is equivalent to that with $C = C_{su}$ on a hypothetical top surface ($z = 2H$) where H is the height of the molten Zry. Therefore, the solution of Jain(45) applies to the present case with H is replaced by $2H$. With this replacement, the solution of Jain can be reduced to

$$\frac{M_t}{M_\infty} = 1 - \left[1 - 2 \left[\frac{\tau_H}{\pi} \right]^{1/2} \right] \left[1 - 4 \left[\frac{\tau_d}{\pi} \right]^{1/2} + \tau_d \right] \quad (D.14)$$

in which $\tau_H = \frac{Dt}{H^2}$, $\tau_d = \frac{4Dt}{d^2}$, $d = 0.5$ cm and $H = 0.5$ cm. Equation (D.14) is plotted as the lower curve in Fig. 4.16.

In order to plot the experimental data at 2200°C , the saturation mass fraction of uranium in molten Zry is needed. From Eq. (G.5), C_{su} at 2200°C is 0.78. Using this value, the experimental data are normalized and plotted in Fig. 4.16.

APPENDIX E : Calculation of the Fractional Volume Decrease of UO_2 Pellet as a Function of UO_2 Content of Molten Cladding

The amount of UO_2 dissolved by cladding is a function of the ratio of the cladding volume to the UO_2 volume. In order to show the effect of this ratio on the UO_2 pellet dissolution in a melt-down event, the percentage of UO_2 pellet volume decrease was calculated as a function of UO_2 content of molten cladding for three typical reactors(PWR, BWR, and CANDU).

The mass of UO_2 dissolved per cm height(m_{UO_2}) is :

$$m_{\text{UO}_2}(\text{g/cm}) = \frac{\alpha C_u M_Z}{1 - C_u} \quad (\text{E.1})$$

in which C_u = mass fraction of uranium(on an oxygen-free basis) in molten cladding, M_Z = mass of cladding per cm height, and α = conversion factor($= \frac{270}{238} = 1.18$).

Using m_{UO_2} , we obtain the volume of UO_2 dissolved per cm height(ΔV_{UO_2}) :

$$\Delta V_{\text{UO}_2}(\frac{\text{cm}^3}{\text{cm}}) = \frac{m_{\text{UO}_2}}{\rho} = \frac{\alpha C_u M_Z}{(1 - C_u)\rho} \quad (\text{E.2})$$

in which ρ = the density of UO_2 (10.96 g/cm³).

Then, Eq. (E.2) is used to obtain the fractional volume decrease of UO_2 pellet :

$$\frac{\Delta V_{\text{UO}_2}}{V_p} = \frac{\alpha C_u M_Z}{(1 - C_u)\rho V_p} \quad (\text{E.3})$$

in which V_p = original volume of UO_2 pellet per cm height.

Table E.1 shows the fuel rod dimensions of three typical reactors. Using these dimensions, M_Z and V_p are calculated and Eq. (E.3) is plotted in Fig. 4.20.

Table E.1 Fuel Rod Data for Three Typical Reactors *

	PWR	BWR	CANDU
Pellet O.D.(cm)	.819	1.056	1.440
Clad O.D.(cm)	.940	1.250	1.520
Clad Thickness (cm)	.057	.086	.038
Clad Weight per cm Height(g/cm)	.921	1.832	1.034
Pellet Volume per cm Height (cm ²)	.532	.881	1.634

* : Data from J. J. Duderstadt and L. J. Hamilton,
 "Nuclear Reactor Analysis," John Wiley & Sons, Inc., 1976

APPENDIX F : Sample Calculation of Dissolution of LWR Fuel

Prior to melting of the Zry cladding, reaction of solid Zry with steam forms a scale of ZrO_2 on the exterior of the cladding. Upon melting of the remaining metallic portion of the cladding, Hagen's experiments shows that the liquid can be held in place by its still-solid skin(47). Alternatively, the film may rupture, permitting the liquid Zry to flow down the rod. Chung and Gehl(48), on the other hand, have proposed a chemical mechanism by which the oxide skin can fail. Neither of these rupture mechanisms is considered here.

When melting takes place, the oxide layer is replenished by continued absorption of oxygen from reaction with the external steam. This process is not affected by melting of the metal inside of the oxide skin. However, the corrosion rate at the steam-oxide interface is known to be strongly influenced by the fraction of hydrogen in steam(steam starvation effect). Consequently, in order to show the effects of the Zry oxidation by steam on the fuel liquefaction, three limiting cases are studied. The fuel rod considered here has the following specifications :

- stoichiometric fuel pellet 1 cm diameter
- cladding 0.7 mm thickness
- at time of melting, the cladding has a 0.06 mm-thick layer of ZrO_2 on the steam side and the average oxygen content of the remaining metal is 2 w/o. The temperature of the cladding increases suddenly to 2100 °C after melting.
- gross fluid motion(i.e., candling) of the melt is neglected.

A) Case I

System :

- the cladding is steam-starved on the outside(i.e., pure H_2 on the outside).
- the ZrO_2 layer remains intact after melting of the metal and does not interact with the

melt during fuel dissolution.

Results :

Since the melt is not oxidized by steam, the time history of the uranium concentration in the melt can be obtained by using Eq. (D.12)(i.e., natural convective transport) with δ [Eq. (D.9)] calculated for the present geometry. This can be regarded as a thin enclosed slab. From Eq. (D.9), δ is calculated as 6.8×10^{-3} cm/s by using $C_{su}=0.46$, $B=0.57$, and $d=0.07$ cm(cladding thickness). Here, C_{su} at 2100°C for the 2.0 w/o O-Zry system is obtained by linear approximation of the asymptotic saturation data for the pure Zry and the 6.0w/o O-Zry systems at 2100°C (Fig. G.2). However, S/V is ~ 15 for the present geometry, as explained in section 4.3. Then, by using these values of δ and S/V , Eq. (D.12) is plotted as curve I-a in Fig. F.1. Also, the history of the uranium concentration in the melt for short times can be obtained by using Eq. (C.3)(i.e., 1-D diffusion in the thin liquid layer). By using $C_{su}=0.46$, $D=3.2 \times 10^{-5}$ cm²/s, and $H=0.07$ cm, Eq. (C.3) is plotted as curve I-b. Note that the maximum time at which Eq. (C.3) is applicable to the present geometry is ~ 10 s. On the other hand, the fractional volume decreases of the UO_2 pellet are calculated by using curves I-a and I-b, respectively, and Eq. (E.3), in which $V_p=0.79$ cm³/cm and $M_Z=1.23$ g/cm were used. The results are shown in Fig. F.2.

B). Case II

System :

- instead of an inert ZrO_2 layer contacting the molten Zry on the side opposite the fuel, the ZrO_2 can dissolve in the molten Zry according to the appropriate phase diagram solubility and with the same mass transfer coefficient used for the fuel side. Alternatively, the ZrO_2 skin can dissolve in the molten Zry according to 1-D diffusion process.

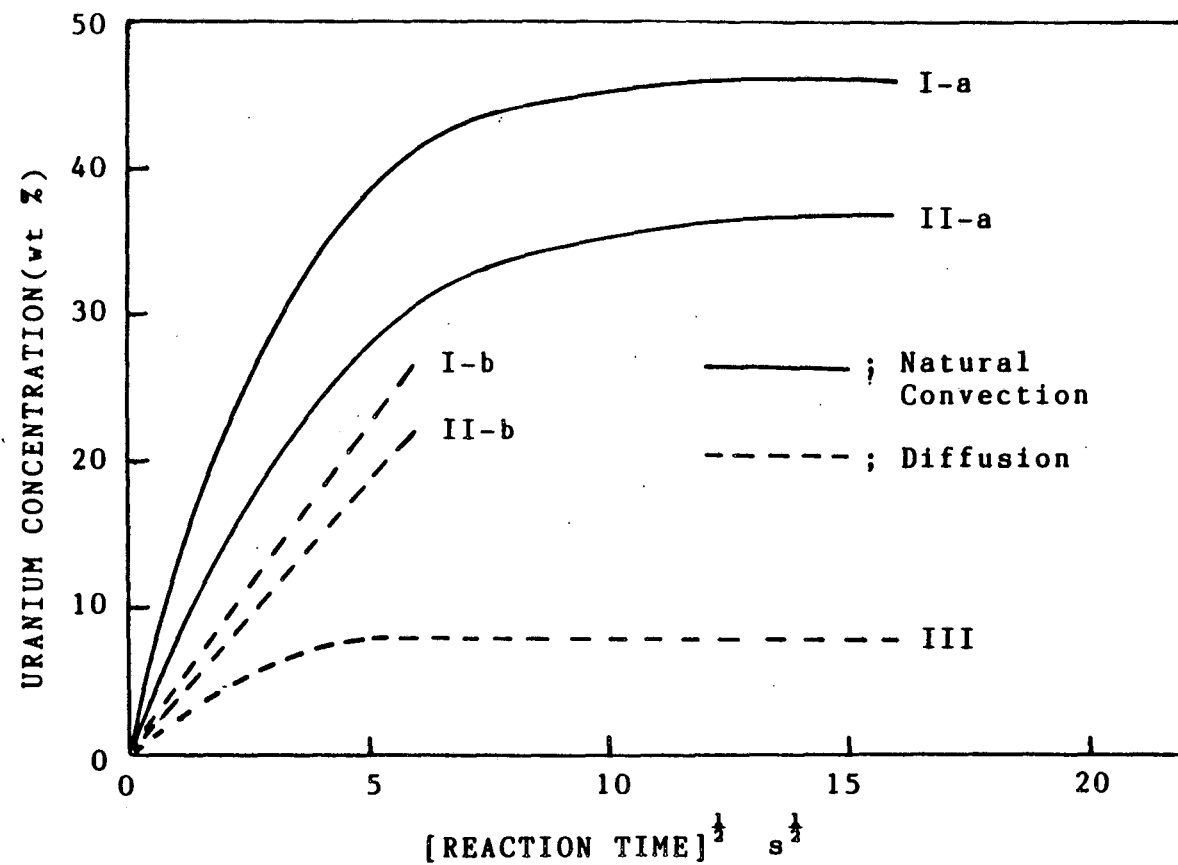


Fig. F.1 Time History of Uranium Concentration in the Zry Melt at 2100°C for Three Limiting Cases.

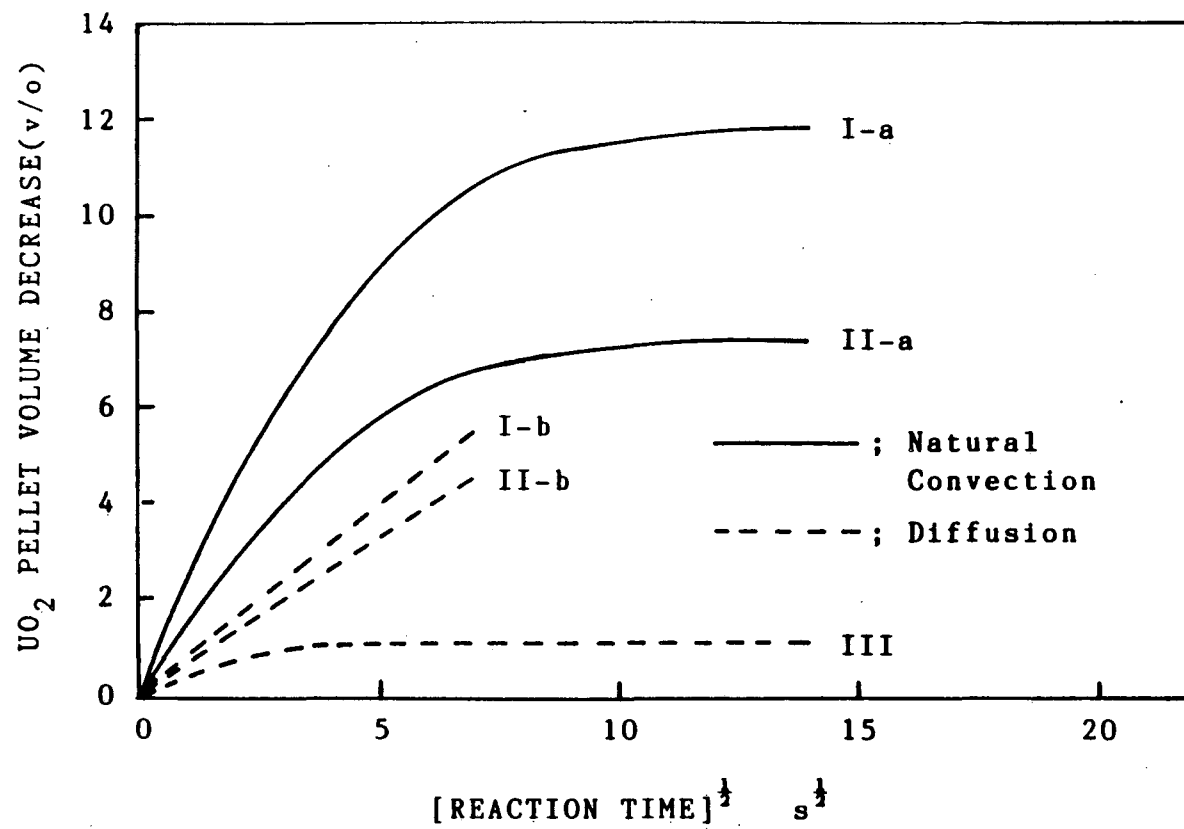


Fig. F.2 Time History of the Fractional Volume Decrease of UO_2 Pellet at 2100°C for Three Limiting Cases.

Results :

From the Zr-O phase diagram, the solubility of oxygen in the Zry melt is ~ 11.3 w/o. By using this value and the same mass transfer coefficient obtained from curve I shown in Fig. F.1, the oxygen concentration in the melt caused by natural convective transport is calculated as a function of time and plotted in Fig. F.3. This figure shows that the oxygen concentration is constant after ~ 1 s (solid line) because there is a limited oxygen source (i.e., thin oxide layer dissolves completely in the melt, prior to substantial fuel melting). Consequently, the initial oxygen content in the melt is assumed to be ~ 3.9 w/o. Then, by using the same method used for plotting curve I-a of Fig. F.1, the time history of the uranium concentration in the melt caused by natural convection is calculated and plotted as curve II-a in Fig. F.1. On the other hand, the time history of the oxygen concentration in the melt caused by 1-D diffusion is calculated by using Eq. (C.3), in which the solubility of oxygen in the melt = 11.3 w/o and the diffusivity of oxygen in the melt = $3.4 \times 10^{-4} \text{ cm}^2/\text{s}$ are used. Here, the diffusivity of oxygen in the melt is taken to be four times larger than in the solid oxide(51). The results are shown in Fig. F.4. This figure shows that the solid oxide is completely dissolved after ~ 1 s. Therefore, the initial oxygen content is assumed to be ~ 3.9 w/o. Then, by using the same method used for plotting curve I-b, the time history of the uranium concentration in the melt caused by 1-D diffusion is plotted as curve II-b in Fig. F.1. Additionally, the fractional volume decrease of the UO_2 pellet is calculated by using curves II-a and II-b, respectively, and Eq. (E.3), in which $V_p = 0.72 \text{ cm}^3/\text{cm}$ and $M_Z = 1.30 \text{ g/cm}$ are used. The results are shown in Fig. F.2.

C) Case III

System :

- steam contains the outside of the ZrO_2 layer and oxygen is formed by decomposition of water and diffusion through the ZrO_2 scale (at a rate given by usual Zry corrosion rate equation).

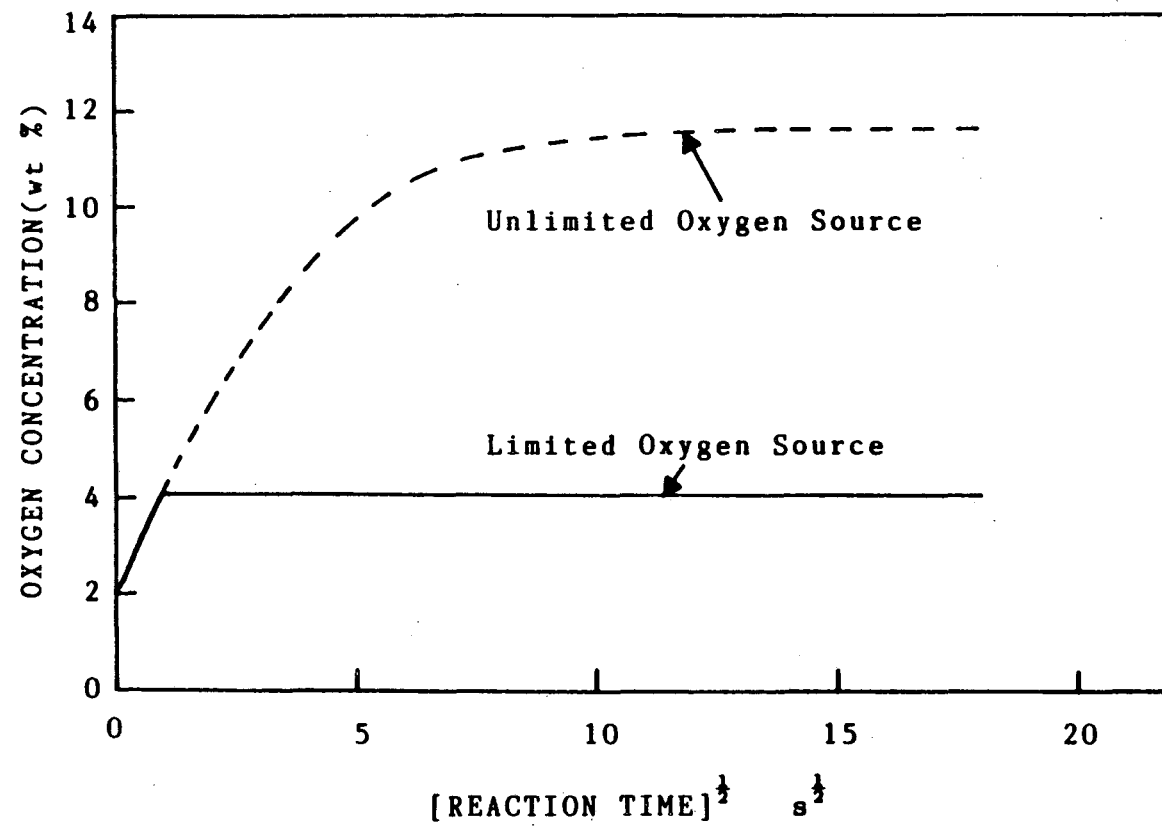


Fig. F.3 Time History of Oxygen Concentration in the Zry Melt Caused by Natural Convection for Case II.

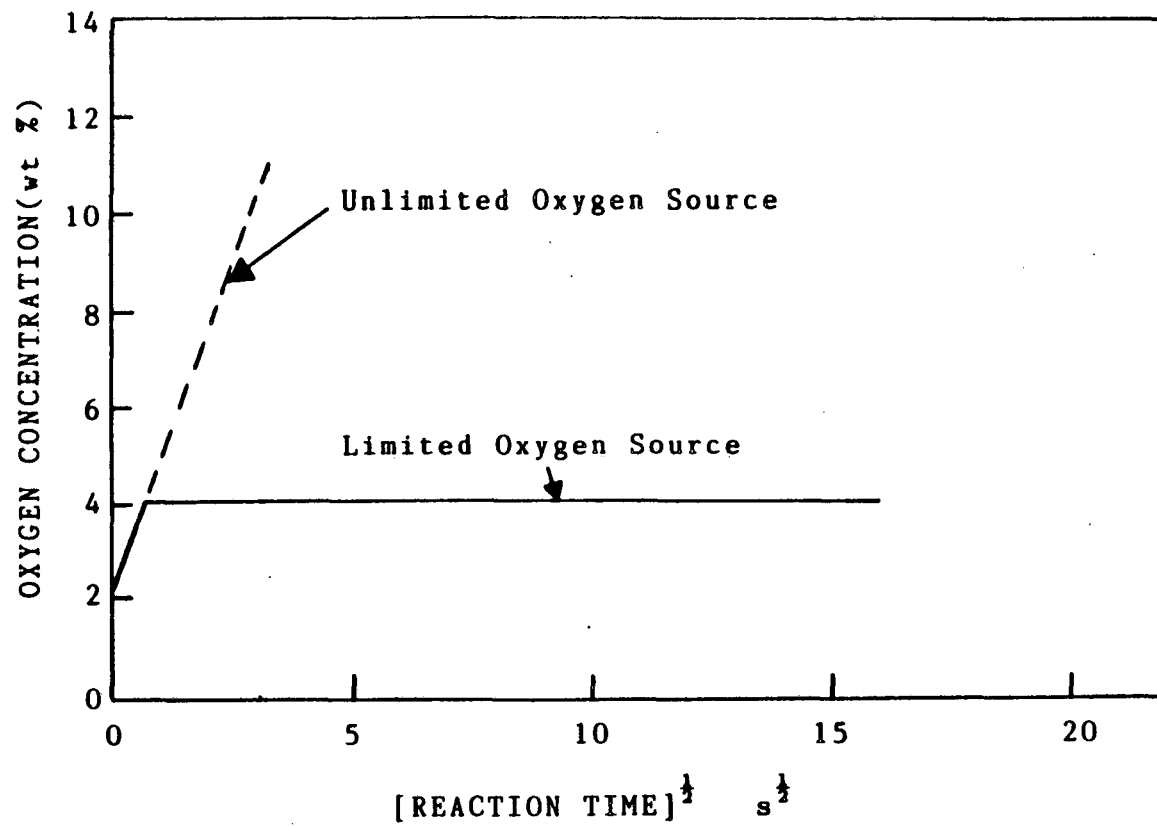


Fig. F.4 Time History of Oxygen Concentration in the Zry Melt Caused by 1-D Diffusion for Case II.

Results :

Detailed analysis of oxidation kinetics of liquid Zircaloy in contact with steam was given by Olander(51). Fig. F.5 shows a schematic diagram for calculating the evolution of an oxide layer contacting a liquid metal. The initial state of system consists of a slab of solid Zircaloy of thickness L_{20} with an average oxygen content C_{20} . Upon melting, the oxygen in the metal is assumed to become homogenized in the liquid so that the concentration is uniform at $t=0$. The thickness of the initial oxide layer is denoted by L_{10} and its composition is assumed to be that of stoichiometric zirconia, which has an oxygen concentration denoted by C_0 . The lower sketch of this figure shows the system after interaction of the liquid metal and the oxide scale. The thickness of the oxide and the liquid metal are L_1 and L_2 , respectively. Oxygen concentration distributions are sketched as heavy lines. The boundary concentrations C_0 , C_a and C_b are obtained from the Zr-O phase diagram at the specified system temperature. Using the two-medium moving-interface diffusion shown in Fig. F.5, Olander calculated oxide layer and metal thickness changes as functions of time following liquefaction of the metal(Fig. F.6). This figure shows the results of the calculation at 2000°C for a specimen with an initial metal-to-oxide thickness ratio of 10. Two extreme values of the initial oxygen concentration in the metal are used, namely, oxygen-free and 98 % saturated.

In the present case, the initial oxygen concentration is 2 w/o and an initial metal-to-oxide thickness ratio is ~ 10 . Therefore, metal thickness changes for the present case are obtained by linear interpolation between the two curves shown in Fig. F.6. The results are shown in Fig. F.7. However, in order to calculate uranium saturation concentrations in the melt, the oxygen increase of the melt from the ZrO_2 oxide dissolution is needed as a function of time. Here, the oxygen content in the melt is assumed to increase parabolically from 2 w/o to 26 w/o(oxygen content of ZrO_2) during a dimensionless time of ~ 1000 (see Fig. F.6), when the entire metal is converted to ZrO_2 . The results are shown in Fig. F.7. Note that this oxygen content neglects the oxygen increase of the melt from fuel dissolution, which

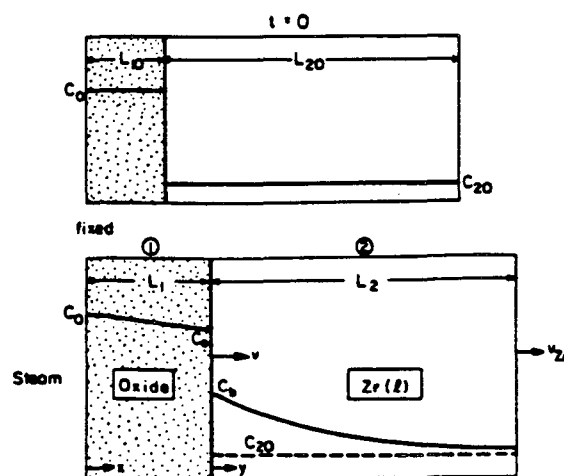


Fig. F.5 Diagram for Calculating the Evolution of an Oxide Layer Contacting a Liquid Metal.

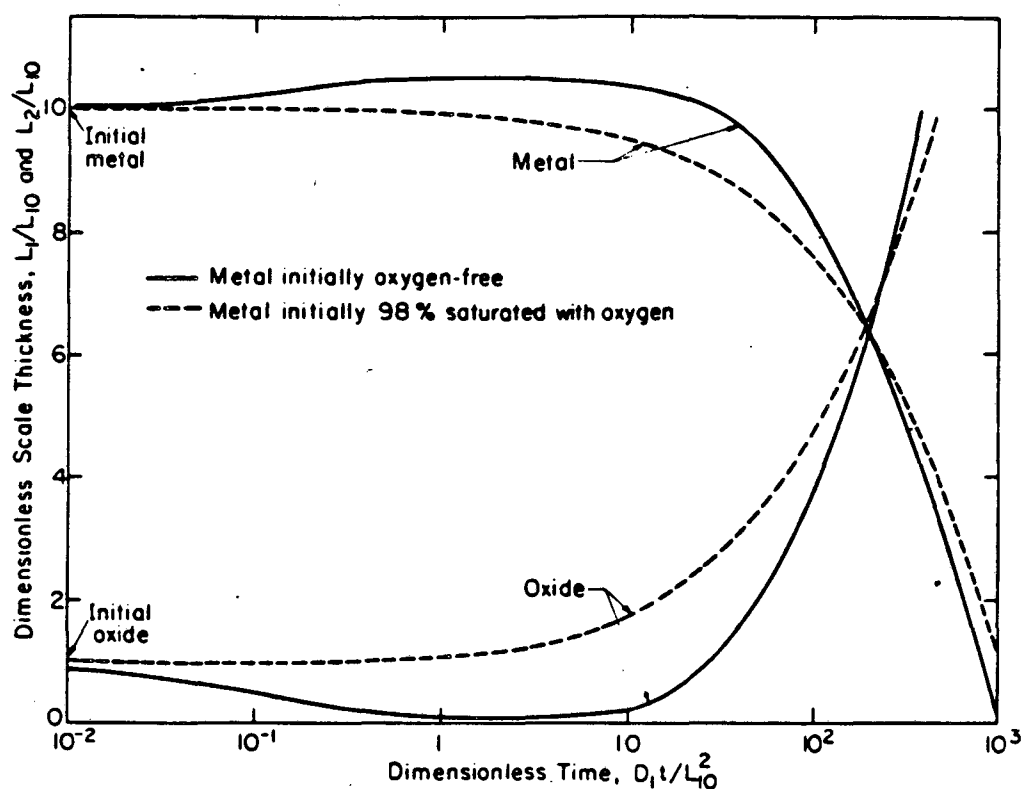


Fig. F.6 Oxide Layer and Metal Thickness Changes as a Function of Time Following Liquefaction of the Metal at 2000°C(51).

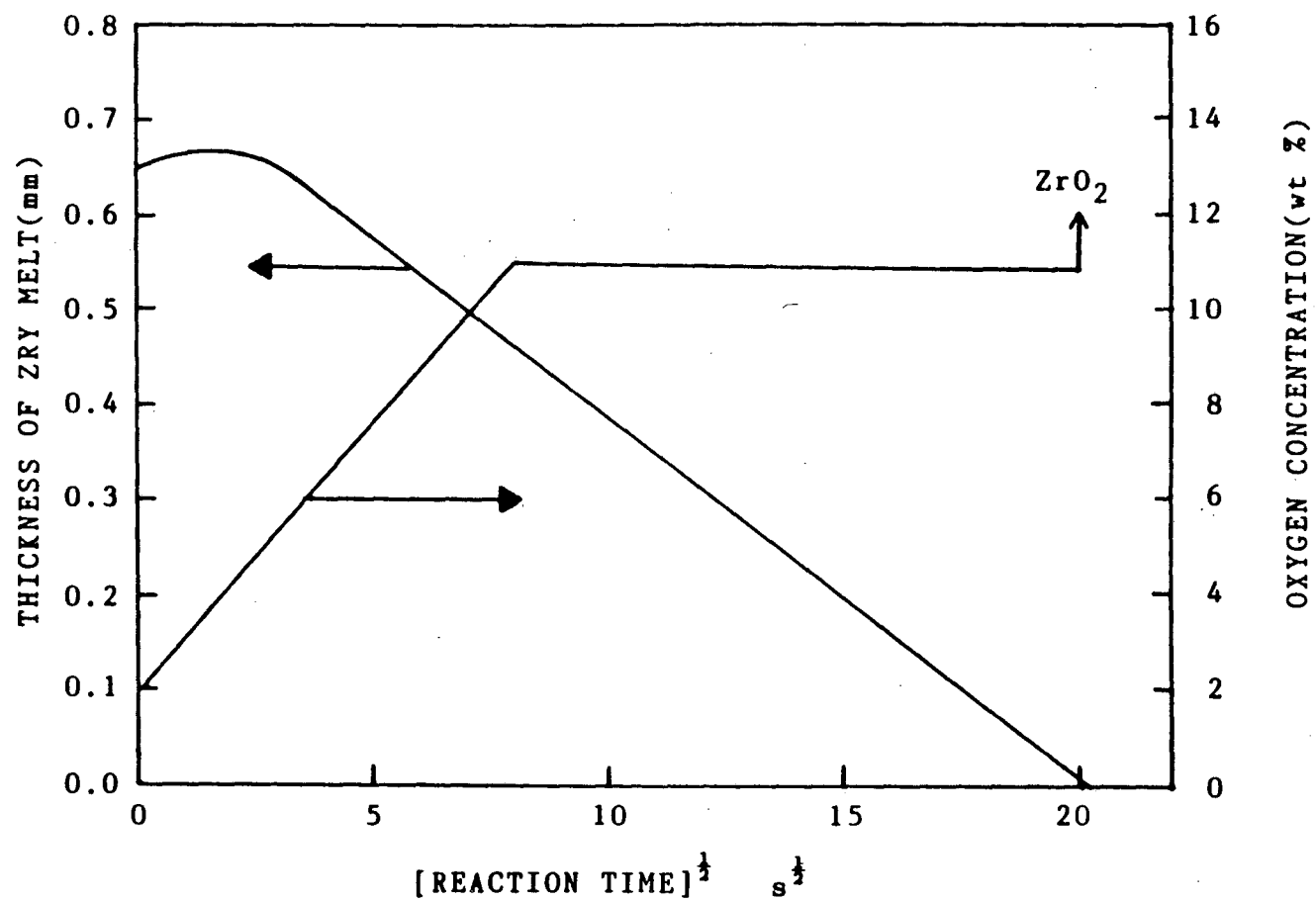


Fig. F.7 Thickness of Remaining Zry Melt and Its Oxygen Concentration versus $[\text{Reaction Time}]^{1/2}$ for Case III.

occurs simultaneously. This figure shows that the oxygen content increases to 11.3 w/o(solubility of oxygen in liquid Zry at 2100°C) at ~50 s. After this time, the oxygen content in the melt is taken to be constant. Then, by using the oxygen increase shown in this figure and linear approximation of the asymptotic saturation data(Fig. G.2), C_{su} is calculated as a function of time and plotted in Fig. F.8. Finally, the time history of the uranium concentration in the melt caused by 1-D diffusion is calculated by using Eq. (C.3) and plotted as curve III in Fig. F.1. Here, the time-dependent values of H and C_{su} (Figs. F.7 and F.8), and $D=3.2 \times 10^{-5} \text{ cm}^2/\text{s}$ are used. Curve III shown in Fig. F.1 indicates that the uranium dissolution stops at a time of ~23 s because the oxygen content in the melt is so large that no more uranium can dissolve. On the other hand, the fractional volume decreases of the UO_2 pellet are calculated by using curve III shown in Fig. F.1 and Eq. (E.3), in which $V_p=0.79 \text{ cm}^3/\text{cm}$ and time dependent M_Z (Fig. F.7) are used. The results are shown in Fig. F.2.

Figs. F.1 and F.2 indicate that the amount of fuel dissolution for natural convective transport is larger than that for diffusion. In addition, the amount of fuel dissolution for case I is the largest while that for case III is the smallest. Therefore, it is concluded that fuel dissolution by liquid Zry depends strongly on the oxygen content of liquid Zry and transport mechanism.

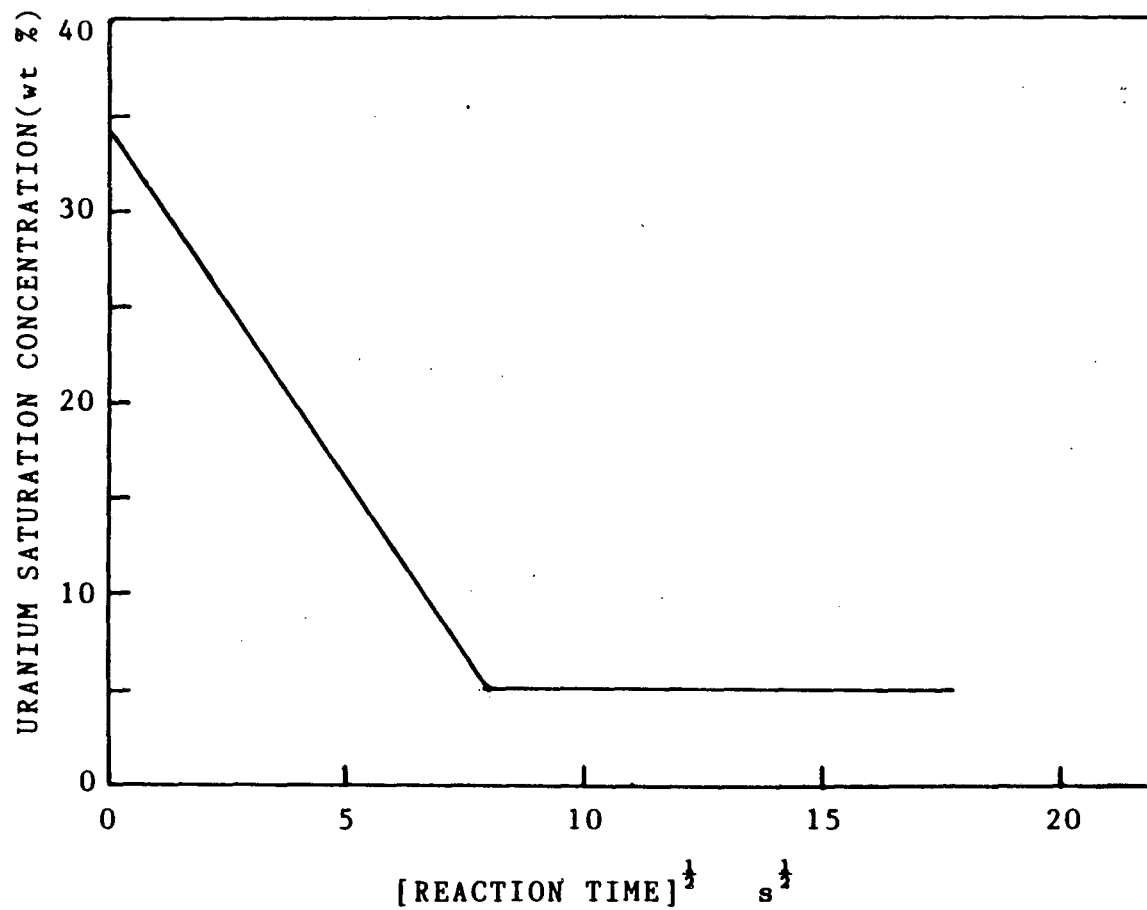


Fig. F.8 Time History of Uranium Saturation Concentration in the Zry Melt for Case III.

APPENDIX G : Equilibrium Considerations

G.1 Introduction

Three measures of the "equilibrium" quantity of uranium dissolved in liquid zirconium are discussed here.

The first is the true equilibrium represented by the boundary between the two-phase zone and the liquid in the ternary phase diagram(Fig. 1.1-g).

The second is the pseudo-binary phase diagram of Fig. 1.2, in particular the boundary between the Zr-rich melt and the two-phase zone. This boundary was determined(4) by isothermally adding stoichiometry UO_2 to Zry which had been saturated with oxygen at $\sim 1200^\circ\text{C}$ (i.e., ~ 30 a/o oxygen). The boundary is determined when the added UO_2 does not completely dissolve in the liquid Zry.

The third measure of equilibrium is the asymptotic uranium concentration(measured by XFS) approached at long contact times in the series of tests with Zry in the UO_2 crucible(Fig. 3.43).

In this Appendix, these three equilibrium measures are compared.

G.2 Comparison of the Pseudo-binary Diagram with the Ternary Phase Diagram at 2000°C .

The boundary between the Zr-rich melt and the two-phase region in the pseudo-binary diagram should be consistent with the corresponding boundary in the ternary diagram. This consistency check is made by adding UO_2 to a fixed quantity of Zry and following the process on the ternary phase diagram shown in Fig. G.1. Point A represents stoichiometric UO_2 and point B represents liquid Zry containing 30 a/o oxygen. The mixture must, by mass balance considerations, lie along the line AB. As UO_2 is added to the Zry, the system moves from B towards A. When point P is reached, the first precipitate of the ternary oxide $(\text{U,Zr})\text{O}_{2-x}$ appears. Its composition is located at point Q, the extremity of the equilibrium tie line starting from P. Since the tie lines are unknown, the point Q is not

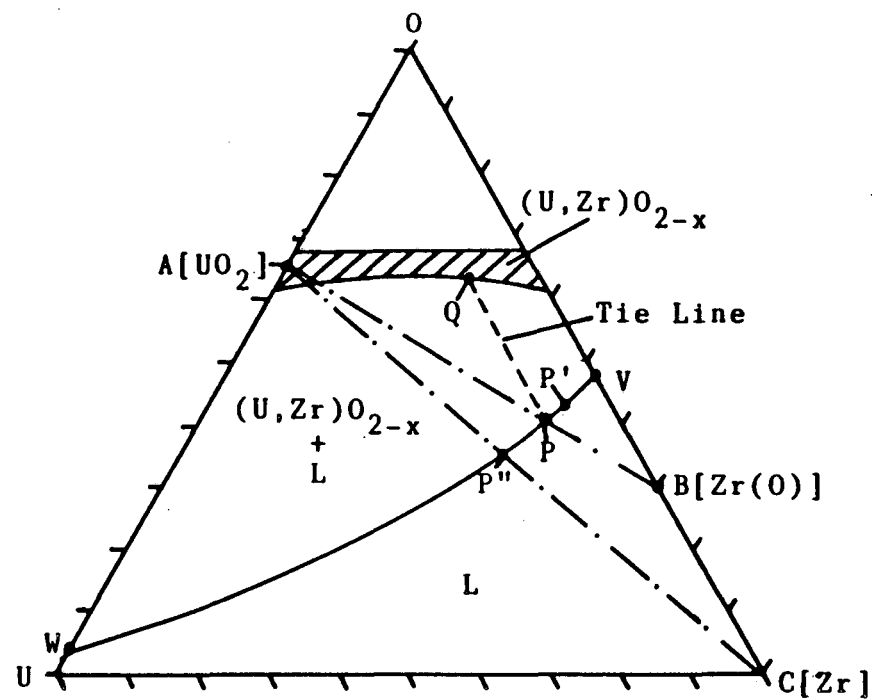


Fig. G.1 Equilibrium Considerations in the U-Zr-O Ternary Phase Diagram at 2000°C.

determined. However, since we are considering only the point at which the oxide phase just begins to precipitate, the quantity of this phase is very small and can be neglected in the following element balances.

Suppose at point P, the melt consists of :

M_z g atoms of Zr

m g atoms of U

n g atoms of O

The atom fraction of uranium on an oxygen-free basis is given by

$$y_{U'} = \frac{m}{m + M_z} \quad (G.1)$$

This quantity is fixed by the lever rule applied to line AB of Fig. G.1 :

$$(y_u)_{Ter} = \frac{PB}{AB} = 0.24$$

The same quantity is also obtainable from the intersection of the 2000°C isotherm with the liquid/two-phase boundary of the pseudo-binary phase diagram(Fig. 1.2). This value is ~0.18 in Skokan's diagram(4) and ~0.09 in Politis' diagram(3). Therefore, there is still inconsistency between the pseudo-binary phase diagram and the ternary phase diagram, concerning the composition of the liquid/two-phase boundary, even though Skokan's diagram shows better agreement than Politis' diagram.

The quantity of oxygen is fixed by the oxygen-to-metal ratios of the initial reactants :

$$n = 2m + \left(\frac{q}{1-q}\right)M_z \quad (G.2)$$

where q = atom fraction of oxygen in Zr(O).

The atom fraction of oxygen in the melt at point P in Fig. G.1 is :

$$y_o = \frac{n}{n + m + M_z} \quad (G.3)$$

Substituting Eqs. (G.1) and (G.2) into (G.3) yields :

$$y_o = \frac{(\frac{q}{1-q})(1-y_{U'})+2y_{U'}}{(\frac{1}{1-q})(1-y_{U'})+2y_{U'}+1} \quad (G.4)$$

G.3 Location of the Saturation Concentration on the Ternary Phase Diagram.

The asymptotic uranium concentrations approached at long contact times(see Fig. 3.43) are plotted as a function of temperature in Fig. G.2. This saturation line is given by :

$$y_{U'} = 1.2 \times 10^3 \exp(-36/RT) \quad (G.5)$$

where $R = 1.987 \times 10^{-3}$ kcal/mole.

Also presented in Fig. G.2 is the single datum representing uranium saturation concentration in molten Zry with 27 a/o oxygen from Fig. 3.43 and the pseudo-solubility line from the pseudo-binary diagram(Fig. 1.2). Below we compare these results.

The saturation limits deduced from Fig. 3.43 are not true equilibrium ratios because the Zr/U ratio in the crucible is not uniform. Rather, a thin layer of ternary oxide forms on the inner crucible wall in contact with the melt(zone A₂). Fig. G.3 depicts the interaction and the nomenclature used in the following analysis. The saturation states of Fig. 3.43 are characterized by the following :

- 1) The crucible in zone A₁ has been reduced to UO_{2-x} on the lower phase boundary of the U-O binary. At 2000°C, the stoichiometry is 1.84(50).
- 2) The ternary oxide layer is sufficiently thin to neglect its contributions of U, O, and Zr to material balances on the system. However, this ternary oxide is connected to the melt composition by an equilibrium tie line on the ternary phase diagram(e.g., point Q in Fig. G.1).

Let m = gram moles of UO₂ dissolved in the liquid at saturation. The saturation concentration of uranium on an oxygen-free basis is given by Eq. (G.1). However, instead of Eq.

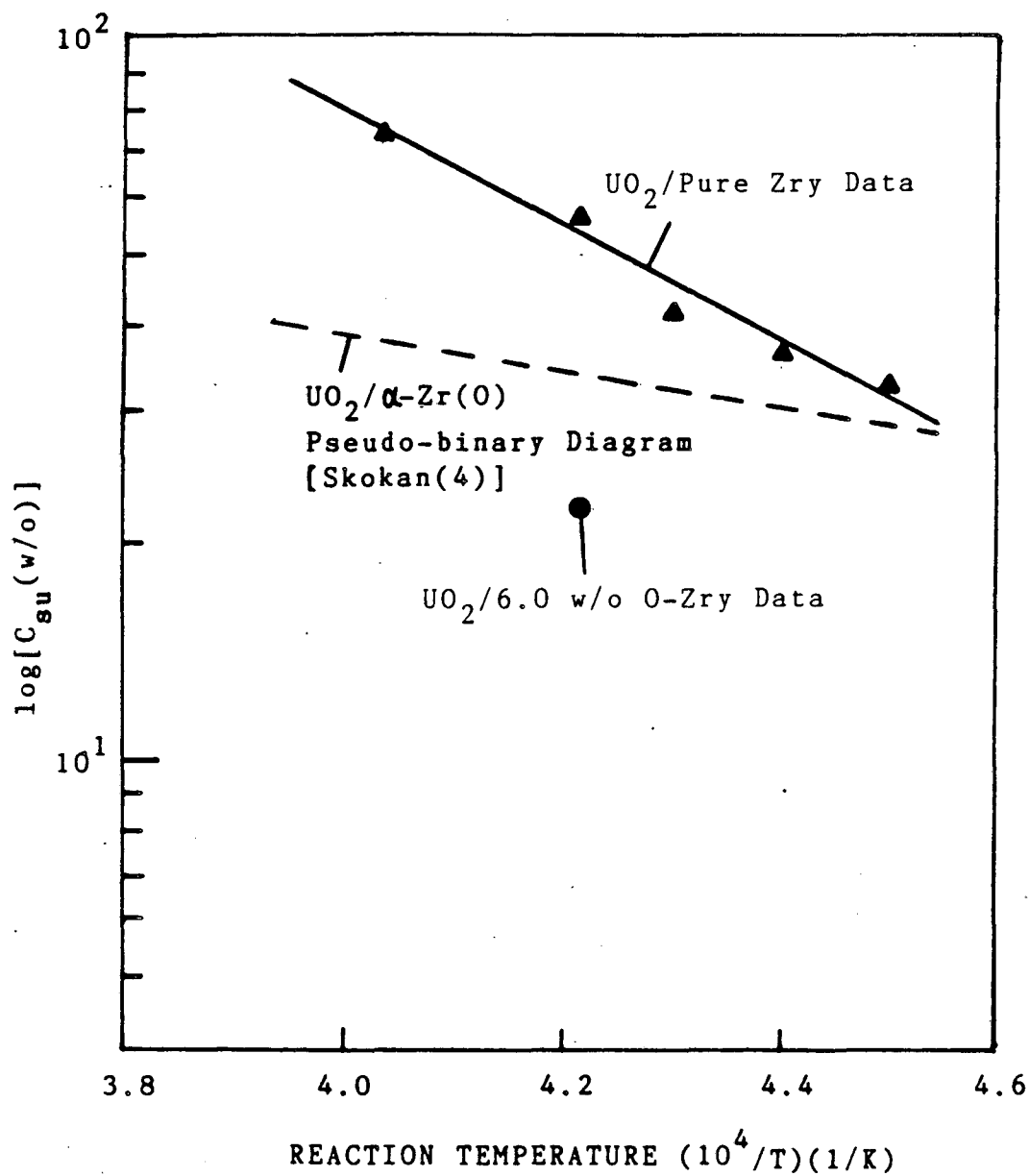


Fig. G.2 Saturation Concentration of Uranium in Zry Melt as a Function of Reciprocal Temperature.

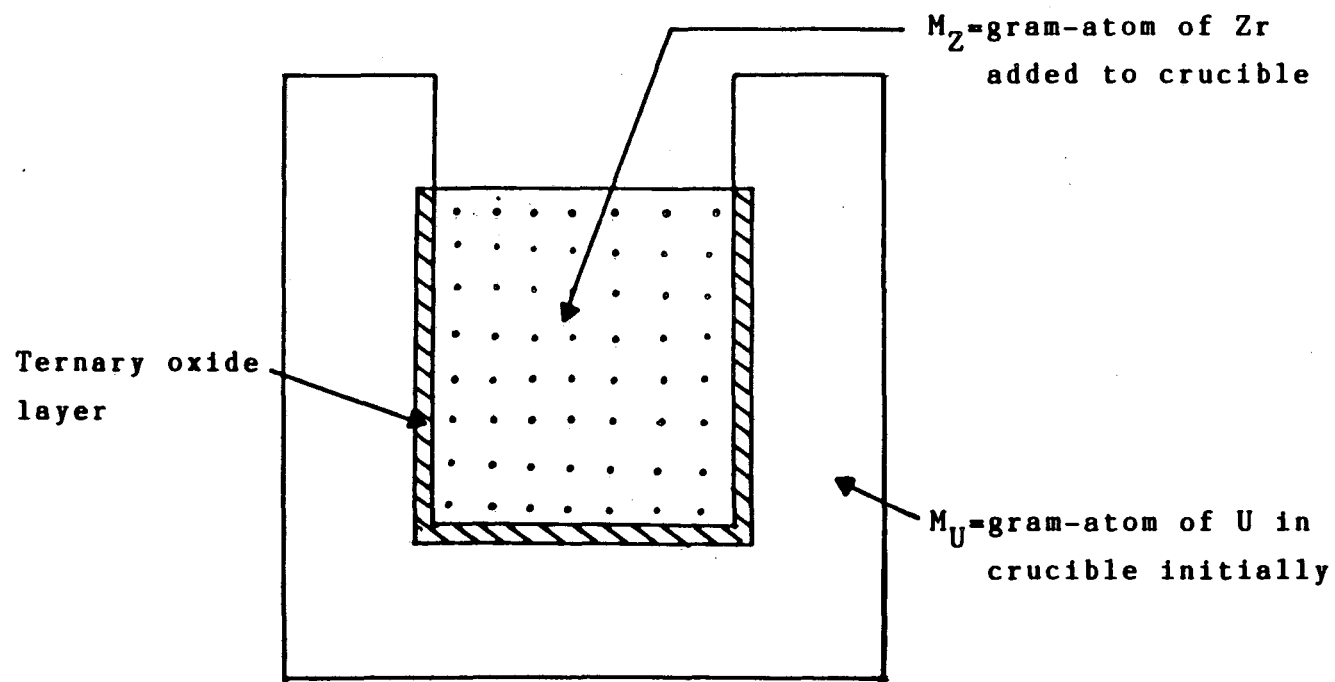


Fig. G.3 A Schematic Diagram of the UO_2 Crucible/Molten Zry System.

(G.2), the number of gram-atom of oxygen in the melt at saturation is :

$$n = 2m + \left(\frac{q}{1-q}\right)M_z + (2-x)(M_U - m) \quad (\text{G.6})$$

The three terms in Eq. (G.6) represent

- 1) Oxygen dissolved along with m in gram-atom of dissolved uranium.
- 2) Oxygen initially in the Zry charge.
- 3) Oxygen added to the melt by reduction of the crucible to UO_{2-x} .

Using Eqs. (G.1) and (G.6) in Eq. (G.3) yields :

$$y_o = \frac{\left(\frac{q}{1-q}\right)(1-y_U') + 2y_U' + (2-x) \left[\frac{M_U}{M_z}(1-y_U') - y_U' \right]}{\left(\frac{1}{1-q}\right)(1-y_U') + 2y_U' + 1 + (2-x) \left[\frac{M_U}{M_z}(1-y_U') - y_U' \right]} \quad (\text{G.7})$$

which differs from Eq. (G.4) by the last term in the numerator and denominator, representing the extra oxygen absorbed from the crucible.

Determination of y_o and y_U' is achieved by combining Eq. (G.7) with the ternary phase diagram shown in Fig. G.1. The lower phase boundary(UV) can be regarded as a giving y_U' as a function of y_o . The saturation point(P') is the simultaneous solution of this phase boundary function and Eq. (G.7). Because of the oxygen supplied by reduction of the crucible, P' need not be on the mass-balance line(i.e., P). The disposition of P' relative to P can be determined as follows. Let

$$a = \left(\frac{q}{1-q}\right)(1-y_U') + 2y_U'$$

$$\Delta = (2-x) \left[\frac{M_U}{M_z}(1-y_U') - y_U' \right]$$

Using these abbreviations, Eq. (G.7) becomes :

$$y_o = \frac{a + \Delta}{a + 1 + \Delta}$$

When $\Delta=0$, P' lies on AB(i.e., at P) and Eq. (G.7) reduces to Eq. (G.4). Also, $y_o(\Delta) > y_o(\Delta=0)$, so P' is always above P, as shown in Fig. G.1.

The behavior exhibited in Fig. G.2 can be qualitatively explained with the help of Fig. G.1. First, we neglect the crucible-reduction contribution, so that the saturated melt is at P in Fig. G.1. As the oxygen content of the initial Zry is reduced, point B moves towards the Zr corner. It can be immediately seen that a line connecting Zr with A(i.e., AC) crosses UV at a point(P'') which represents a larger concentration of uranium. This explains why the saturation data plotted in Fig. G.2 for the UO_2 /pure Zry system lie above the dashed line representing Skokan's(4) pseudo-binary solubilities for the UO_2 /Zr(O) system, in which the Zry initially contained 30 a/o oxygen.

The single datum shown in Fig. G.2 represents uranium saturation concentration of the Zry initially with 27 a/o oxygen which is just a bit less oxygen than the Zry used in constructing the pseudo-binary diagram. Therefore, the point B on Fig. G.1 was located at approximately the same position in these two cases. However, there was no additional oxygen added to the melt in the latter case($\Delta=0$), whereas in the former, reduction of the UO_2 crucible supplied extra oxygen not available in the pseudo-binary experiments. As a result, the saturation concentration in the crucible saturation experiment is at P' while the pseudo-binary melt is at P. The point P' has a lower uranium fraction(lever rule) than P, which explains why the point in Fig. G.2 the UO_2 crucible saturation result for 6 w/o-O Zry falls below the pseudo-binary solubility at the same temperature.

G.4 Summary

We conclude from the above analyses that the asymptotic saturation data observed in the UO_2 crucible/Zry kinetic studies are internally consistent(i.e., prior oxygen addition to the Zry). These data are also in qualitative agreement with the ternary phase diagram, and the difference from the pseudo-binary phase diagram is satisfactorily rationalized.

For kinetic analysis of the dissolution process, Eq. (G.5) provides the uranium concen-

tration in the liquid at the solid surface needed to characterize the mass transport flux.

7. REFERENCES

1. S. Hagen, "Out-of-pile Bundle Temperature Escalation under Severe Fuel Damage Conditions," OECD-NEA-CSNI/IAEA Specialists Meeting on Water Reactor Fuel Safety and Fission Products Release in Off-Normal and Accident Conditions, RISO National Laboratory, Denmark, May, 1983
2. P. Hofmann and D. K. Kerwin-Peck, "UO₂/Zircaloy-4 Chemical Interactions and Reaction Kinetics from 1000 to 1700°C under Isothermal Conditions," KfK3552, Nov. 1983
3. C. Politis, "Investigation of the Ternary Uranium-Zirconium-Oxygen System," KfK2167, 1975
4. A. Skokan, "High Temperature Phase Relations in the U-Zr-O System," 5th Int. Meeting on Thermal Nuclear Reactor Safety, Karlsruhe, Germany, Sep. 1984
5. S. Yamanaka, M. Katsura, M. Miyake, S. Imato, and S. Kawasaki, "On the Reaction between UO₂ and Zr," J. Nucl. Mater., 130, 1985, 524
6. W. G. Hutchings and H. E. Rosinger, "The UO₂/Zircaloy-4 Interaction : A Metallographic Examination," ASM Metal Congress, Michigan, U.S.A., Sep. 1984
7. P. Hofmann and H. J. Neitzel, "Experimental and Theoretical Results of Cladding Oxidation under Severe Fuel Damage Conditions," 7th Int. Conference on Zirconium in the Nuclear Industry, Strasbourg, France, June, 1985
8. P. Hofmann, D. Kerwin-Peck, and P. Nikolopoulos, "Physical and Chemical Phenomena Associated with the Dissolution of Solid UO₂ by Molten Zircaloy-4," 6th Int. Conference on the Zirconium in the Nuclear Industry, Vancouver, British Columbia, June, 1982
9. P. Hofmann, "Dissolution of Solid UO₂ Fuel by Molten Zircaloy-4 Cladding," SFD Program Review Meeting, Oak Ridge, U.S.A., April, 1986
10. H. A. Saller and F. A. Rough, J. M. Fackelmann, A. A. Bauer, and J. R. Doig, "Phase Relations in the Uranium-Zirconium-Oxygen System Involving Zirconium and Uranium Dioxide," BMI-1023, 1955 11.

11. M. W. Mallett, J. W. Droege, A. F. Gerds, and A. W. Lemmon, Jr., "The Zirconium- UO_2 Reaction," BMI-1210, July, 1957
12. D. R. Olander, "The UO_2 /Zircaloy Chemical Interaction," J. Nucl. Mater., 116, 1983, 271
13. A. Denis and D. Garcia, "Model to Describe the Interaction between UO_2 and Zircaloy in the Temperature Range 1000 to 1700°C," J. Nucl. Mater., 116, 1983, 44
14. R. G. Schwind and G. C. Vliet, "Observations and Interpretations of Natural Convection and Stratification in Vessels," Proc. Heat Trans. Fluid Mech. Inst., 51, 1964, 52
15. J. A. Clark, "A Review of Pressurization, Stratification and Interfacial Phenomena," Adv. Cryogen. Eng. 8, 1964, 259
16. B. D. Neff and C. W. Chiang, "Free Convection in a Container of Cryogenic Fluid," Adv. Cryogen. Eng. 12, 1966, 117
17. L. B. Evans, R. C. Reid, and E. M. Drake, "Transient Natural Convection in a Vertical Cylinder," A.I.Ch.E. 14(2), 1968, 251
18. H. Z. Barakat and J. A. Clark, "Analytical and Experimental Study of the Transient Laminar Natural Convection Flows in Partially Filled Liquid Containers," Int. Heat Trans. Conf., 2, 1966, 152
19. C. F. Hess and C. W. Miller, "Natural Convection in a Vertical Cylinder Subject to Constant Heat Flux," Int. J. Heat Mass Trans., 22, 1979, 421
20. Bird, Stewart and Lightfoot, "Transport Phenomena," John Wiley and Sons, 1960
21. J. H. Chin, E. Y. Harper, S. E. Hurd, A. M. Levy, and H. M. Satterlee, "Analytical and Experimental Study of Liquid Orientation and Stratification in Standard and Reduced Gravity Fields, July 1, 1963 through May 31, 1964," NASA Contract NASA-11525, Lockheed Missiles and Space Company, May, 1964
22. D. C. Elrod, G. E. Giles, and W. D. Turner, "HEATING6 : A Multidimensional Heat Conduction Analysis with the Finite-Difference Formulation," NUREG/CR-0200, Vol 2, Section F10, ORNL/NUREG/CSD-2/V2, Oct., 1981

23. P. G. Shewmon, "Transformations in Metals," McGraw-Hill, 1969
24. M. C. Fleming, "Solidification Processing," McGraw-Hill, 1974
25. J. D. Livingston and H. E. Cline, Trans. AIME, 245, 1969, 351
26. P. Hofmann, D. Kerwin-Peck, and P. Nikolopoulos, "Explanation of the UO_2 /Zircaloy-4 Reaction Layer Sequence in Terms of the Total Interfacial Energy of the System," J. Nucl. Mater., 124, 1984, 114
27. D. R. Uhlmann, B. Chalmers, and K. A. Jackson, J. Appl. Phys., 35, 1964, 2986
28. G. W. Roper and D. P. White, "Interdiffusion in Two-Phase Ternary Solid Systems," Metal Sci., 15, 1981, 148
29. J. B. Clark and F. N. Rhines, "Diffusion Layer Formation in the Ternary System Aluminum-Magnesium-Zinc," Trans. ASM, 51, 1959, 193
30. J. S. Kirkaldy and L. C. Brown, "Diffusion Behavior in Ternary, Multi-Phase Systems," Canadian Metall. Quart. 2, 1963, 89
31. J. Meijering, Discussion to Reference 29
32. D. Glasser-Leme and H. Matzke, "Interdiffusion and Chemical Diffusion in UO_2 - (U, Pu) O_2 System," J. Nucl. Mater., 106, 1982, 211
33. D. K. Reimann and T. S. Lundy, J. Am. Ceram. Soc., 52, 1969, 511
34. J. O'M. Bockris, J. L. White and J. D. Mackenzie, "Physico-Chemical Measurements at High Temperatures," Butterworths, London, 1959
35. N. H. Nachtrieb, "Liquid Metals, Chemistry and Physics," New York, Marcel Dekker, 1972
36. J. F. Elliott and M. Gleiser, "Thermochemistry for Steelmaking," Reading, Mass., Addison-Wesley, 1963
37. M. Kawakami and K. S. Goto, Trans. Iron Steel Inst. Jpn., 16, 1976, 204
38. I. A. Novokhatskii and G. S. Ershov, Izv. Akad. Nauk. SSSR, Met., 2, 1967, 43
39. K. Suzuki and K. Mori, J. Iron Steel Inst. Jpn., 57, 1971, 2219
40. G. S. Ershov and V. M. Bychev, Izv. Akad. Nauk. SSSR, Met. 1, 1975, 6

41. P. M. Shurigin and V. I. Kryuk, *Izv. Akad. Nauk. SSSR, Metall. Gorn.Delo*, 3, 1963,94
42. P. M. Shurigin and V. I. Shantarin, *Izv. VUZ Chernaya Metall.*, 12, 1964, 10
43. R. Yang, J. Hovingh, E. Leborgne, and D. R. Olander, "Diffusion of Lanthanum in Liquid Uranium," *High Temp. Sci.* 7, 1975, 55
44. J. S. Finucane and D. R. Olander, "The Viscosity of Uranium and Two Uranium-Chromium Alloys," *High Temp. Sci.* 1, 1969, 466
45. S. C. Jain, "Simple Solutions of the Partial Differential Equation for Diffusion," *Proc. Roy. Soc.(London)*, A243, 1957, 1234
46. G. B. Wallis, "One-Dimensional Two-Phase Flow," McGraw-Hill, 1969
47. S. Hagen and H. Malauscheck, *Trans. Amer. Nucl. Soc.* 33, 1979, 505
48. H. M. Chung and S. M. Gehl, "Thermochemical aspects of fuel rod material interactions at 1900°C," *Int. Meeting on Thermal Nuclear Reactor Safety, Chicago, Sep., 1982*
49. R. E. Pawel, J. V. Cathcart, and R. A. McKee. *J. Electro-chem. Soc.* 125, 1979, 1105
50. R. K. Edwards and A. E. Martin, "Oxygen-Uranium Phase-Equilibrium System," *Symposium Proceedings on Thermodynamics, Vienna, July 1965*
51. D. R. Olander, "Oxidation of Liquid Zircaloy by Steam," *J. Nucl. Mater.*, 119, 1983 245
52. P. Hofmann, Personal Communication

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