DOE/ET/11439-T2

MTR

~~F 1339~~
FIA503 ER 01339
76

March 26, 1980

Final Report

CHEMISTRY OF ZIRCONIUM RELATED TO THE BEHAVIOR OF
NUCLEAR FUEL CLADDING

MASTER

Principal Investigator:

Daniel Cubicciotti

Prepared for:

U.S. Department of Energy
Division of Basic Energy Sciences
Washington, D.C. 20545

Technical Monitor:

Dr. Robert P. Epple
Division of Materials Sciences
ER-152; MS J-309, GTN

DOE Contract No. ~~EY-76-S-03-1339~~

SRI Project PYU 5780

AC03-77ET 11439

Approved:

R. W. Bartlett

R. W. Bartlett, Director
Materials Research Laboratory

P. J. Jorgensen, Vice President
Physical and Life Sciences

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

SRI International

333 Ravenswood Ave. • Menlo Park, California 94025
(415) 326-6200 • Cable: SRI INTL MPK • TWX: 910-373-1246

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MGW

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

The following pages are an exact
representation of what is in the original
document folder.

CONTENTS

SUMMARY OF ACTIVITIES	1
Objective	1
Summary of Results	1
PROGRESS IN THIS FIELD	4
Research in this Field	4
Models for PCI/SCC Failures	5
Chemical Aspects of Mechanism	7
PUBLICATIONS	9
REFERENCES	10
APPENDICES	

- A Thermodynamics of Zirconium Iodides at Elevated Temperatures
- B Thermodynamics of the Gaseous Zirconium Iodides *removed pub. lit.*
- C The Chemistry of the Zirconium-Iodine System
- D Thermodynamics of Vaporization of ZrI_4 in the Univariant Region: Zirconium Monoiodide/Zirconium
- E Thermodynamics of Vaporization and High Temperature Enthalpy of Zirconium Tetraiodide *removed pub. lit.*
- F Thermodynamics of Vaporization of ZrI_4 from Substoichiometric Solid Zirconium Iodides
- G Thermodynamic Properties of the Solid Zirconium Iodides
- H Chemisorption of Iodine on Zirconium
- I Initial Stages of Oxidation of Zirconium
- J. Vapor Transport of Zirconium and Silicon during Heat Treatment in Silica *removed - pub. lit.*
- K Chemical Aspects of Iodine-Induced Stress Corrosion Cracking of Zircalloys

SUMMARY OF ACTIVITIES

Objective

The objective of the project was stated in the original proposal as follows:*

The objective of the proposed program is to generate basic information on zirconium chemistry that is needed to understand the behavior of Zircaloy-clad nuclear fuel rods. In pursuit of this objective, studies of the chemistry of the zirconium-iodine and zirconium-oxygen systems will be undertaken to elucidate their thermodynamics and kinetics. It is anticipated that the results obtained will lead to an improved understanding of the chemical processes involved in chemically assisted fuel rod failures.

This project has been very productive in generating information on zirconium chemistry, as the results show. Not only have we classified the thermodynamics of both the gas phase and the solids in the zirconium-iodine system, we have provided valuable information on the chemisorption of iodine and of oxygen on zirconium surfaces at high temperatures. In addition, we have studied the kinetics of reactions on zirconium surfaces. These results have already been helpful in understanding the stress corrosion cracking of Zircaloy, and we believe these findings will be useful to future researchers in this field.

Summary of Results

The results of this project, presented in detail in the appendices, which include copies of all publications, are summarized below.

(1) Gas Phase Chemistry

- We have shown that several suspected gaseous iodides exist, namely ZrI_4 , ZrI_3 , ZrI_2 , and ZrI . Except for ZrI_4 , no one had ever directly observed any of these species. They were only inferred to exist (see Appendix A).

*SRI Proposal No. PYU 75-313, November 15, 1975.

- The heats of formation of all four species were measured by our mass spectrometric technique (see Appendix B).
- The results showed that the estimated information in the literature was so far wrong that its use led to entirely erroneous interpretations of chemical processes involving gaseous zirconium iodides--namely, the iodide process for refining and the vapor phase mechanism for SCC of Zirconium (see Appendix A).

(2) Solid State Chemistry

- We have shown that there are four solid compounds in the system, corresponding roughly in composition to ZrI_4 , ZrI_3 , ZrI_2 , and ZrI . Prior evidence for the first three existed. We have shown that ZrI exists and that it is the lowest iodide--that is, the first solid to form on a zirconium metal surface (see Appendices C and D).
- Torsion effusion studies were used to determine the thermodynamics of vaporization of ZrI_4 and hence the enthalpy of formation of gaseous ZrI_4 and the absolute entropy of the solid (see Appendix E).
- The same experimental technique was used to delineate the regions of two solid phase equilibria in the system and evaluate the thermodynamics of vaporization of ZrI_4 from the solids as a function of composition (see Appendices D and F).
- The enthalpies of formation of solid ZrI_3 , ZrI_2 , and ZrI were derived from a thermodynamic treatment of the system as a whole (see Appendix G).

(3) Chemisorption of Iodine on Zirconium

- An Auger study of zirconium heated in a flux of iodine gas showed that iodine was chemisorbed in the clean zirconium surface even at rather high temperatures (see Appendix H).
- An assessment of the thermodynamics of the chemisorption, based on the thermodynamics of both the gaseous species and solid compounds that we determined in items (1) and (2) above, showed that the enthalpy of formation of the chemisorbed layer was the same as that of solid ZrI but the entropy of the chemisorbed state was much larger (see Appendix H).

(4) Initial Stages of Oxidation of Zirconium

An Auger study of the surface of a zirconium crystal heated in low pressures of oxygen showed that, even under conditions where the surface appears clean, there is a surface oxide. The mechanism of oxidation in that regime, in which the kinetics obey a linear oxidation law, involves diffusion of oxygen through the oxide surface layer of constant thickness (see Appendix I).

(5) Influence of Residual Fluoride on Zircaloy Heat Treatments

If a Zircaloy specimen is heat treated in a sealed silica bulb, the surface of the specimen usually becomes coated with silicides. This procedure has often been used for metallurgical heat treatments. We have shown that vapor transport of silicon and zirconium both occur and that this vapor transport is due to traces of residual fluoride on the metal surface resulting from fluoride pickling treatments (see Appendix J).

(6) Stress Corrosion Cracking (SCC) of Zircaloys

- A vapor phase mechanism for removal of zirconium from the tip of an SCC crack through the cyclic action of gaseous zirconium subiodides is not viable because we have shown that the gaseous subiodides are not important species in the pertinent environment (see Appendix K).
- The minimum amount of iodine required to produce SCC of Zircaloy has been reported in the literature. Our results show that under those conditions the largest part of the iodine will react with the zirconium to form solid ZrI and possibly some solid ZrI_2 . Therefore, the mechanism of SCC probably involves surface diffusion of iodide to the tip of the advancing crack (see Appendix K).
- Our chemisorption studies show there is a significant driving force for the transfer of iodide from the lowest solid iodide (ZrI) to the fresh metal surface generated by crack advance (see Appendix K).

PROGRESS IN THIS FIELD

Research in This Field

The objective of this project was to provide chemical information that would help elucidate a certain type of nuclear fuel rod failures. Mechanical and chemical interactions between the UO_2 fuel pellets and the Zircaloy cladding of light water-cooled reactor (LWR) fuel rods can result in cladding failures. Pellet-cladding interaction (PCI) failures tend to occur in rods that have been irradiated to significant burnup and then subjected to power increases.^{1,2} It is now generally agreed that this type of fuel failure is due to stress corrosion cracking of the cladding.^{3,4} Cracking, usually on a radial plane, originates at the inside surface of the cladding and is thought to result from hoop tensile stresses and strains imposed on the cladding by fuel thermal expansion during the power ramp and by chemical attack of aggressive fission products released from the UO_2 fuel.⁴ Iodine, an abundant fission product, has long been known to promote SCC of Zircaloys at reactor operating temperatures and is one of the prime suspects as the chemical substance involved in PCI-SCC cladding failures.⁴

Research addressing the overall problem of PCI failures is too broad to be pertinent to the present discussion. For example, such research programs include investigations of the following: the effects of reactor operation (power ramping); changes in the geometry of the UO_2 pellets; methods for changing the release of fission products from the UO_2 ; lubricants and/or barriers in the fuel clad group; and metallurgical modification of the Zircaloy cladding.

We are concerned with understanding the mechanism of SCC of zirconium alloys. In this area of research, which is a fraction of the overall research field, two closely intertwined aspects of the mechanism need to be considered: (1) the mechanical metallurgy of the process and (2) the

chemical interactions between the environment and the metal as it is being strained. Progress in this area is reported in several recent publications.⁵⁻⁷

Models for PCI/SCC Failures

The status of our understanding of chemically assisted cracking of Zircalloys can best be illustrated by quoting two models for the process, which have recently been described in the literature.

One model, presented by Roberts et al.,⁵ is summarized in the following excerpts from that reference:

The basis for this model is that PCI fracture of LWR fuel rods is caused by stress corrosion cracking (SCC), with the fission product iodine being the responsible chemical species. Justification for this starting point is the physical appearance of the cracks found in power reactor fuel rods following PCI events. The characteristics of the fracture surfaces examined in light water reactor fuel rods are typical of SCC fractures produced in laboratory iodine SCC tests.

The results of experimental studies support a model of iodine-induced SCC failure of Zircaloy cladding tubes that is similar to that proposed by Cox and Wood. Our model consists of four stages--oxide penetration, crack formation, crack propagation, and cladding rupture.

We believe that the threshold stresses observed in the tube pressurization tests are associated with crack formation because the minimum stress for continued growth of a pre-existing stress corrosion crack is expected to decrease with increasing crack depth. The theoretical analysis supports this conclusion. Therefore, we regard crack formation as the critical step in the iodine-induced failure of internally pressurized Zircaloy tubes.

Crack propagation occurs by a mixture of cleavage and ductile tearing (fluting) in stress-relieved materials but may involve intergranular processes in unirradiated, recrystallized material. Our theoretical analyses are based on the former mode of propagation, since it is the faster of the two processes. Stress corrosion crack propagation continues until plastic instability occurs, resulting in rapid, ductile fracture of the uncracked ligament ahead of the crack, usually on a shear surface.

Theoretical Analyses. Two experimental observations form the basis for the theoretical analyses. First, a transgranular

crack forms in the vicinity of a preexisting small flaw at the cladding surface when the Zircaloy is stressed sufficiently during a power ramp. In our laboratory experiments, the flaw was either an inclusion or a precipitate particle, but a fabrication defect or a grain boundary could also be activated. Second, we consider two mechanisms by which material fails as the crack grows. Environmentally assisted cleavage occurs in grains so oriented that the hoop stress resolved in the direction normal to the near-basal cleavage plane is sufficiently large; the remaining grains fracture by a plastic (ductile) process. The combination of these two failure mechanisms is what gives rise to the characteristic fluted fracture surface. The local strain for cleavage fracture should be smaller than that for plastic rupture, and the fracture process zone is, therefore, a region in which a fraction of grains have failed by cleavage, while the remaining grains still support a load; thus, the fracture process zone is a region of partial loss of cohesion. Therefore, fracture is viewed as being a sequential process in which the cleavage grains first fail so as to overload the fluting grains, which then fail in turn and allow a true crack to propagate.

The authors then developed a mathematical treatment that is not relevant here.

Another model for SCC failure was presented by Yaggee et al.⁶ The pertinent aspects are as follows.

The results described have been used to derive a model to describe the physical processes involved in iodine SCC of Zircaloy. The model is based on the observations that iodine SCC failures usually begin as intergranular fractures that change to cleavage and fluting fractures at some point in crack growth. It is assumed that these two modes of fracture involve different mechanisms of crack growth. It is further assumed that the intergranular fracture is due to chemical attack, which is essentially independent of applied stress, while the cleavage and fluting fracture can be described by fracture mechanics.

It is unlikely that the intergranular crack growth would be completely independent of stress. In fact, stress-assisted chemical attack may be necessary to prevent blunting of the crack tip. However, because no information is available concerning the effect of stress on intergranular chemical attack in Zircaloy, stress effects are not considered at this time. The time to failure in an SCC test can thus be divided into the time to chemically grow an intergranular crack plus the time to propagate the crack to failure by cleavage and fluting.

The chemical aspects of intergranular crack growth are difficult to develop phenomenologically since many chemical and kinetic reactions may be involved. Because of the difficulties of a first-principles derivation, an empirical relation that satisfies the required boundary conditions for chemical crack growth was developed. The assumed boundary conditions to be satisfied are as follows: the initial growth rate of the crack at the inner surface due to chemical attack has some finite value and the crack-growth rate due to chemical attack decreases with crack depth, reaching a value of zero for a crack of infinite depth.

Chemical Aspects of Mechanism

Consideration of these models indicates that the chemical aspects are not well treated. The results we obtained concerning the thermodynamics of the zirconium-iodine system have been useful; however, most of the information that we obtained on this project has not been published and therefore has not been incorporated into proposed mechanisms.

There are still aspects of the chemistry that need further investigation. In particular, the kinetics of reactions between iodine and zirconium and their effect on the kinetics of crack initiation and crack propagation need to be determined. The second model for SCC discussed above calls for information about the crack growth rate due to chemical attack. The thermodynamic information we obtained lays the groundwork for a proper investigation of the kinetics by specifying the conditions under which various phases or chemisorbed states are stable.

Another area in which information is needed for good modeling is the surface diffusion rate of iodine chemisorbed on zirconium. We have shown that chemisorption is important and that there is a strong thermodynamic driving force for iodine to be transported to fresh zirconium at a crack tip. The rate of transport may determine the crack propagation rate; therefore surface diffusion rate information is important.

Another important chemical aspect of the SCC problem concerns the site of initiation of cracks. The initiation process is very important in both models discussed above. There is little information about the mechanism of initiation. We found that in commercial Zircaloy tubing

failures often occur at sites in the metal surface that have high concentrations of impurities (e.g., iron is frequently found). Information about the chemistry of the Fe-Zr-I system would further our understanding of that phenomena. In particular, we need to know the rates of reactions of such alloys with iodine compared with pure zirconium and whether there are solid ternary iodides that are more stable than zirconium monoiodide.

PUBLICATIONS

The papers resulting from this contract are listed below in chronological order and include both those that have been published and those in the process of being published. Copies of the complete papers are appended.

- D. Cubicciotti, K. H. Lau, and M. J. Ferrante, "Thermodynamics of Vaporization and High Temperature Enthalpy of Zirconium Tetraiodide," *J. Electrochem. Soc.*, 125, 972 (1978).
- P. D. Kleinschmidt, D. Cubicciotti, and D. L. Hildenbrand, "Thermodynamic of the Gaseous Zirconium Iodides," *J. Electrochem. Soc.*, 125, 1543 (1978).
- D. Cubicciotti, D. L. Hildenbrand K. H. Lau, and P. D. Kleinschmidt, "Thermodynamics of Zirconium Iodides at Elevated Temperatures," in Proceedings of the Symposium on High Temperature Metal Halide Chemistry, edited by D. L. Hildenbrand and D. Cubicciotti The Electrochemical Society, Inc., Princeton, N.J., 1978).
- D. Cubicciotti, K. H. Lau, "Thermodynamics of Vaporization of ZrI_4 from Substoichiometric Solid Zirconium Iodides," *J. Electrochem. Soc.* 126, 771 (1979).
- D. Cubicciotti, "The Chemistry of the Zirconium-Iodine System," in Specialist Meeting on Internal Fuel Rod Chemistry, Report IWGFPT/3 (International Atomic Energy Agency, Vienna, Austria, 1979).
- D. R. Knittel and D. Cubicciotti, "Vapor Transport of Zirconium and Silicon During Heat-Treatment of Zircaloy in Silica," *J. Electrochem. Soc.*, 125 (1980).
- D. Cubicciotti and K. H. Lau, "Thermodynamics of Vaporization of ZrI_4 in the Univariant Region: Zirconium Monoiodide/Zirconium," to be submitted to *J. Electrochem. Soc.*
- G. N. Krishnan, B. J. Wood, and D. Cubicciotti, "Initial Stages of Oxidation of Zirconium," to be submitted to *J. Electrochem. Soc.*
- R. H. Lamoreaux and D. Cubicciotti, "Thermodynamic Properties of the Solid Zirconium Iodides," to be submitted to *J. Electrochem. Soc.*
- D. Cubicciotti, R. L. Jones, and B. C. Syrett, "Chemical Aspects of Iodine-Induced Stress Corrosion Cracking of Zircaloys," to be submitted to "Zirconium in the Nuclear Industry, Fifth International Conference," *Am. Soc. for Testing Materials*.
- G. N. Krishnan, B. J. Wood, and D. Cubicciotti, "Chemisorption of Iodine on Zirconium at High Temperatures," to be submitted to *J. Electrochem. Soc.*

REFERENCES

1. B. Cox and J. C. Wood, "Iodine Induced Cracking of Zircaloy Fuel Cladding, p. 275 in Corrosion Problems in Energy Conversions and Generation, C. S. Tedmon, Jr., Editor, The Electrochemical Society, Inc., Princeton, New Jersey, 1974.
2. J.A.L. Robertson, in Proc. Joint ANS/CNA Topical Meeting Commercial Fuel Technology Today, Toronto, Canada, April 28-30, 1975, p. 2.2.
3. J. H. Davies et al., in Proc. ANS Topical Meeting Water Reactor Fuel Performance, St. Charles, Illinois, May 9-11, 1977, p. 230.
4. J.T.A. Roberts, E. Smith, N. Fuhrman, and D. Cubicciotti, Nucl. Technol., 35, 131 (1977).
5. J.T.A. Roberts, R. L. Jones, D. Cubicciotti, A. K. Miller, H. F. Wachob, E. Smith, and F. L. Yaggee, "A Stress Corrosion Cracking Model for PCI Failures in LWR Fuel Rods," in Zirconium in the Nuclear Industry, Fourth International Conference, ASTM, STP 681, p. 285, Am. Soc. Test Mats. Philadelphia, PA, 1979.
6. F. L. Yaggee, R. F. Mattas, and L. A. Neimark, "Characterization of Irradiated Zircalloys: Susceptibility to Stress Corrosion Cracking," EPRI Report NP 1155, Electric Power Research Institute Palo Alto, September 1979.
7. Anon., "Proceeding of the ANS Topical meeting on Light Water Reactor Fuel Performance," Portland, Oregon, American Nuclear Soc. Inc., La Grange Park, Illinois, 1979.

PROCEEDINGS OF THE SYMPOSIUM ON
HIGH TEMPERATURE
METAL HALIDE CHEMISTRY

Edited by

D. L. Hildenbrand
SRI International
Menlo Park, California

D. D. Cubicciotti
SRI International
Menlo Park, California

ELECTROTHERMICS AND METALLURGY DIVISION

Proceedings Volume 78-1

THE ELECTROCHEMICAL SOCIETY, INC., P.O. Box 2071, Princeton, N.J. 08540

THERMODYNAMICS OF ZIRCONIUM IODIDES AT ELEVATED TEMPERATURES

D. Cubicciotti, D. L. Hildenbrand, K. H. Lau, P. D. Kleinschmidt

SRI International
Menlo Park, California 94022

ABSTRACT

The chemistry of the zirconium iodides is important in at least two technological areas: the iodide process for vapor refining zirconium and the iodine-induced stress corrosion cracking of Zircalloys. However, the properties of condensed and vapor phases in the Zr-I system have not been sufficiently well established so that the equilibrium behavior of the system can be predicted. In the present study, the thermodynamics of the gaseous zirconium iodides have been determined by a mass spectrometric study of equilibrium partial pressures. The gaseous species ZrI_4 , ZrI_3 , ZrI_2 , and ZrI were all observed, and their enthalpies of formation and bond dissociation energies were derived. The enthalpy of formation of ZrI_4 , which served as a reference for those of the other species, was established from a redetermination of the sublimation thermodynamics by a torsion effusion-weight loss method. The partial pressure of ZrI_4 over lower valent solid iodides also was measured by the torsion effusion method and the stoichiometry of the lower valent iodides determined.

The predominant equilibrium vapor species over all condensed phases in the Zr-I system was found to be ZrI_4 . That information, together with the thermodynamics of the gases, was applied to the iodide vapor refining process to draw interesting conclusions. The information is as yet not sufficiently complete to draw useful conclusions about the stress corrosion cracking of Zircalloys.

INTRODUCTION

The iodide process for refining zirconium involves the formation and transport of gaseous zirconium iodides. The mechanism of the process has not been properly understood because the stabilities of the gaseous iodides were unknown. In fact, the gaseous iodide believed to transport zirconium was incorrectly chosen, based on incorrect thermodynamic information; the latter is corrected in the present paper. In the iodine-induced stress corrosion cracking of zirconium alloys, the mechanism may involve formation of solid zirconium iodides but too little is known about their chemistry to provide any insight into the mechanism. We are investigating the thermodynamics of the gaseous and condensed zirconium iodides to help understand those processes. This paper summarizes our results to date. Detailed reports of the work will be published in the literature.

GASEOUS ZIRCONIUM IODIDES

There is very little literature information about the gaseous iodides. The tetraiodide ZrI_4 is known, but there do not seem to be any experimental observations of even the existence of the gaseous lower iodides, much less their relative stabilities. Although the JANAF Tables (1) list estimated thermochemical properties for the gaseous lower iodides, our mass spectrometric equilibrium data show the values to be in error.

Zirconium Tetraiodide

We have studied the vaporization of solid ZrI_4 by a torsion effusion-weight loss method (2) which provided information about the molecular weight of the evaporating species as well as the vapor pressure. The observed molecular weight was equal to that of ZrI_4 within a few percent; therefore it was concluded that the vaporization reaction was congruent and produced only monomeric ZrI_4 . Our results were in good accord with the higher temperature data of Rahlfs and Fischer (3) and the two sets of data were treated by the second law sigma method with free energy functions given in the JANAF Tables to derive the enthalpy and entropy of the sublimation reaction:

The values obtained were: $\Delta S_{298}^\circ = 47.1$ cal/mol degree; $\Delta H_{298}^\circ = 31.97$ kcal/mole. The sublimation pressure itself can be represented by the equation:

$$\log p, \text{ atm} = 9.57 - 6700/T$$

The enthalpy of formation of gaseous ZrI_4 can be calculated from the measured value for the solid with the resultant value $\Delta H_f(ZrI_4, g, 298 K)$ equal to -84.9 kcal/mole. With that value and the standard entropies for the gas, calculated from measured structural and spectroscopic information (1), the thermodynamic stability of ZrI_4 can be evaluated as a function of temperature. A complete report of this work has been submitted for publication (2).

Lower Iodides

The stabilities of the lower gaseous iodides, relative to the tetraiodide, were determined from equilibrium measurements made by mass spectrometry. The molecular species were generated by the reaction of $HI(g)$ with $Zr(s)$ in effusion cells fitted with gas inlet tubes at the base. Graphite cells were used for studies of ZrI_2 , ZrI_3 , and ZrI_4 at 1100 to 1500 K, while measurements on ZrI at 2200 to 2400 K were made with molybdenum cells.

Identification of the gaseous iodide neutrals was made from the threshold appearance potentials of the ions observed as the experimental conditions were varied. It was possible to identify all of the potential gaseous species, namely ZrI_4 , ZrI_3 , ZrI_2 , ZrI , and Zr under various conditions. The lowest thresholds for ZrI_4^+ , ZrI_3^+ , ZrI^+ , and Zr^+ are approximately equal to the expected ionization potentials of the corresponding neutrals, and clearly establish the presence of these species. ZrI_4 initially appeared at a cell temperature of about 700 K, ZrI_3 at 1100 K, and ZrI , and Zr at about 2200 K. Although the corresponding parent ion threshold for ZrI_2^+ was not observed, at about 1400 K a weak threshold for ZrI^+ appeared at 10 eV, and this was attributed to dissociative ionization of ZrI_2 ; the abundance of the diiodide proved to be substantially lower than any of the other gaseous iodides. The observed threshold appearance potentials are summarized in Table 1.

Neutral abundances and equilibrium data were derived from the ZrI_4^+ , ZrI_3^+ , ZrI^+ , and Zr^+ parent ion intensities, and from the ZrI^+/ZrI_2 fragment ion intensity, measured under conditions that excluded overlap from interfering fragmentation processes. Ion abundance measurements were made by a pulse counting method which made it possible

to obtain reliable data for the less abundant species such as ZrI_2 , ZrI , and Zr .

The equilibria studied are listed in Table 2. In each case the partial pressure of HI was varied by changing its flow rate through the effusion cell. In that way, the partial pressures of the gaseous reactants were varied and the constancy of the mass law expression was tested for each of the equilibria studied. In Reaction (3) of Table 2, there is the same number of gaseous molecules on each side of the equation; therefore instrument sensitivity constants cancel in the mass law expression and it can be evaluated directly from the measured ion intensities. For the other three reactions, the mass law expressions included an instrument sensitivity factor. That factor was determined by calibration against the established vapor pressure of gold.

The equilibrium constants derived from the experimental data were treated by a third law analysis to derive the reaction enthalpy changes. The basis for the third law analysis is the relation:

$$\Delta H_{298}/T = R \ln K - \Delta(G_T^\circ - H_{298})/T$$

In this work, values for the last term (the free energy function) were calculated from estimated molecular constants. The structures and ground state multiplicities of ZrI_3 , ZrI_2 , and ZrI were estimated by analogy with related molecules (1, 4), while the vibration frequencies were estimated from an analysis of the measured values for ZrI_4 and by comparison with the spectroscopic constants of structurally similar molecules. Detailed information will be published (5). It was possible to study reactions (1), (2), and (4) over relatively wide temperature ranges. The resulting second law slope heats are in excellent agreement with the corresponding third law values, providing strong support for the estimated molecular constant assignments.

The third law enthalpies of formation of the four gaseous iodides from the elements in the reference states as used in the JANAF Tables, namely the elemental solids are given in Table 3. (The values from the JANAF Tables are given in parentheses to indicate the errors in those values).

The bond dissociation energy (BDE) for a gaseous molecule is the enthalpy change of the reaction in which one atom is separated from the molecule. The reactions involved in the bond dissociations of the zirconium iodides and the BDE are given in Table 4. The electronic

states of the uncombined electrons on the product molecules are given in parentheses.

The bond dissociation reactions for removal of each of the first three iodine atoms consists of breaking a Zr-I bond which leaves an unpaired electron on the Zr nucleus. However, the ground state of Zr(g) is a $(4d^25s^2)$ state having two paired valence electrons and two unpaired (6). The lowest state in which all the electrons are unpaired is a $(4d^35s^1)$ state that is at an energy of 13.9 kcal/mol above the ground state. If we consider dissociation of ZrI to Zr in that state, the dissociation energy of ZrI is 86.5 kcal/mol (and the average bond dissociation energy becomes 86 kcal/mol). Thus comparison of the four bond dissociation energies for equivalent reactions (which increase the number of unpaired electrons on the Zr by one) shows that they are all within 6 kcal/mol of the average.

Thus the four bond dissociation energies are roughly equal to the average bond energy for complete dissociation of the tetraiodide, when the electronic state of the metal atom is considered. That correlation may provide a useful guide for estimation of bond dissociation energies of other polyatomic metal halides.

The differences among the individual values of the bond dissociation energy reflect differences in the bonding of molecules. Complete understanding of the bonding requires detailed information that is currently unavailable, however, some general comments can be made. The bond dissociation energy for ZrI_4 , i.e., $D(\text{I}_3\text{Zr-I})$, is particularly small, probably because of repulsion between iodine atoms. In the tetrahedral ZrI_4 there are six I-I repulsions at a distance of 4.34 Å; so the electrostatic repulsion amounts to about 460 kcal/mol or 115 kcal/per bond. For trigonal planar ZrI_3 , assuming that the Zr-I distance is 2.66 Å, there are three I-I repulsions at 4.60 Å which amount to 216 kcal/mol or 72 kcal per bond. Thus qualitatively, at least, the electrostatic repulsion between iodide ions can account for the low value for ZrI_4 .

If one assumes the bonds in these gaseous molecules are ionic, a more extensive treatment of their energies can be made. Following the treatment used by Cubicciotti (8), the bond energies are assumed to consist of coulombic and polarization attractive terms and an overlap repulsion term. In Table 5 are given the reactions representing the complete ionization of the gaseous molecules, the equations for the energies of the molecules on the ionic model, calculated energies and the measured ones. The agreement between the calculated energies (U)

from this ionic model are in surprisingly good agreement with the experimentally measured energies (ΔH). For ZrI the polarizability of Zr^{+1} was estimated to be equal to that of Zr^{+2} . The contribution of the Zr polarizability is negligible in the other molecules. The Zr-I internuclear distances were all assumed to be equal to the observed value in ZrI_4 (2.66 Å). That assumption is probably worst for ZrI . Until we have measured values for the internuclear distance, there is little point to speculate further about the validity of the ionic model for the molecules.

APPLICATION TO THE IODIDE PROCESS

The chemistry of the iodide process for refining zirconium has been considered by Shapiro (10). He calculated the partial pressures of the various zirconium iodides from the available estimated data. Figure 1 shows the partial pressures calculated from the JANAF estimates which are roughly the same as those used by Shapiro. From that calculation ZrI_2 remains the predominant species from about 800 to 1800 K; on that basis it is difficult to understand the observed deposition of zirconium at filament temperatures of 1300 to 1800 K. Shapiro remarked about that difficulty and questioned the validity of the thermodynamic data.

The pressures of species calculated from our measured values are shown in Figure 2 for a total iodine pressure of 10^{-4} atm, typical of iodide refining process conditions. These results lead to a simple interpretation of the deposition of Zr in the iodide process based on the thermodynamic data. At low temperatures the major gaseous species is ZrI_4 , whereas at temperatures about 1300 K the major species is I. Therefore, in the iodide process gaseous ZrI_4 is formed from reaction of impure Zr with iodine at low temperatures. The ZrI_4 diffuses to the hot filament and is decomposed to solid Zr and gaseous I atoms. The temperature above which deposition occurs on the hot filament is about 1300 K from the thermodynamic data in Figure 2, in reasonable agreement with experience in the iodide process. Therefore the data indicate that in the iodide process the only important gaseous species are ZrI_4 and I.

The effect of pressure of total iodine-containing species is interesting and can be seen in Figures 3 and 4. The major species under all conditions are either ZrI_4 or I. For one atmosphere total pressure, shown in Figure 3, the temperature at which the ZrI_4 and I pressures cross is about 2200 K. That is, deposition of Zr would occur

only at filament temperatures higher than 2200 K. For total pressures of iodine species of 10^{-8} atm shown in Figure 4 the cross over temperature is about 900 K. Therefore as the pressure of total iodine containing species in the system is increased, the minimum temperature for decomposition of ZrI_4 increases.

In the iodide process it has been observed (11, 12) that as the temperature of the impure zirconium was increased the rate of deposition of Zr first increased then decreased. That behavior can be explained by the effect of pressure on the decomposition temperatures shown in Figures 2 to 4. The initial increase in rate occurs because increasing the temperature of the impure Zr increases the partial pressure of ZrI_4 and thus its rate of arrival at the filament. As the impure Zr temperature is further increased, the fraction of the ZrI_4 arriving at the filament which is decomposed decreases, in accord with Figures 2 to 4, and the decomposition rate falls off largely because that fraction decreases. Shelton (13) discussed the maximum in the rate of the process in terms of changes in the iodine diffusivity and the change in fraction decomposed is implicit in his treatment. We feel it is dominant but otherwise concur with Shelton.

SOLID ZIRCONIUM IODIDES

The solid iodides have been studied by Shelton and coworkers (14) and by Corbett and coworkers (15). The tetraiodide is the highest oxidation state and is well known. Lower iodides are less well characterized and are difficult to prepare. Reactions of the metal with higher iodides or iodine to form lower iodides are very slow so that nonequilibrium mixtures containing unreacted metal are often formed. Corbett et al. found from x-ray diffraction studies that the triiodide phase exists over a large range of stoichiometry from $ZrI_{2.83}$ to $ZrI_{3.43}$ (15). They also found a phase of about $ZrI_{1.9}$ and have determined the structure of a distinct phase, Zr_6I_{12} .

Shelton et al. (14, 16) studied the vapor pressure of ZrI_4 over various Zr-I compositions by an effusion method. We are conducting similar studies. We find from our combined vapor pressure-molecular weight measurements that the only important gaseous species formed from all compositions studied is ZrI_4 . If a sample, initially containing less I than ZrI_4 , is allowed to decompose in an effusion cell suspended from a recording microbalance, measurements of composition as well as pressure can be made. Because ZrI_4 is the effusing gas, the solid gradually changes composition, becoming less rich in iodine.

Effusion pressures are reproducible in certain ranges of composition which presumably correspond to regions in which two solid phases coexist, in accord with phase rule consideration. Therefore regions of homogeneous solid solution can be identified between the regions of two solid phase equilibria.

Shelton et al. (16) find that mixtures of $ZrI_{3.2}ZrI_{3.0}$ give reproducible pressures as do mixtures of $ZrI_{2.8}$ and $ZrI_{1.6}$. We find somewhat different results, in particular, that mixtures of $ZrI_{1.8}$ and $ZrI_{1.5}$ give pressures like those of Shelton et al. for $ZrI_{2.8}$ plus $ZrI_{1.8}$ mixtures. In addition, we find a region of homogeneous solid solution between $ZrI_{1.8}$ and $ZrI_{0.9}$. The $ZrI_{0.9}$ phase loses ZrI_4 vapor to form a phase with less iodine than $ZrI_{0.5}$, which has not yet been characterized. A summary of the phases observed by various workers is given in Figure 5.

The reaction of zirconium with iodine has been found to be slow and nonequilibrium products are obtained in general unless extremely long reaction times are employed. That fact is shown dramatically in the scanning electron microscope photo in Figure 6, which shows the surface of a Zircaloy sheet which had been exposed at 400°C to iodine for 30 hours. Most of the ZrI_4 formed had sublimed away. The surface of the sample is covered by a layer of granular ZrI_4 , and in addition there are crystals of ZrI_4 , $ZrI_{1.7}$, and $ZrI_{0.18}$, and unreacted Zr. That is, there are five solid phases present and it is unlikely that more than two are in equilibrium with the gas. We speculate that on the Zr there is a duplex layer of $ZrI_{0.18}$ under $ZrI_{1.0}$ that is difficult to penetrate so the sublayers (Zr and $ZrI_{0.18}$) are not in rapid equilibrium with the gas. The ZrI and $ZrI_{1.7}$ were probably in equilibrium with gaseous ZrI_4 . The ZrI_4 needles were probably deposited on the surface during cool down. Additional observations of that type are in progress.

APPLICATION TO SCC OF ZIRCONIUM

An objective of our work is to understand the chemistry of the system under conditions of iodine stress corrosion cracking (SCC) of Zircalloys (17). The information discussed above indicates that the only important gaseous iodide in equilibrium with zirconium metal is ZrI_4 . Therefore it is likely in the SCC of Zircalloys that iodine is converted to zirconium iodide and the mechanism of cracking involves the iodides of zirconium and not iodine itself. It has been suggested

(18) that crack propagation may occur by a vapor transport mechanism in which gaseous ZrI_4 is formed at the crack tip and diffuses away to react with oxygen and reform iodine. The net effect is to remove Zr from the crack tip and result in crack propagation. In another type of mechanism it is proposed that a zirconium iodide surface layer is adsorbed at the crack tip. The adsorbed iodine atoms serve to weaken the bonds in the zirconium metal. Bonds at the crack tip, where stresses are greatest are more easily ruptured in the presence of an adsorbed layer of iodide.

Our studies of the pressures of ZrI_4 over the iodide in equilibrium should permit evaluation of the free energy of formation of the lowest iodide and perhaps some estimates of the surface adsorption of ZrI_4 on the metal. The SEM observations are very interesting in this connection because they indicate that the phase that contains the smallest proportion of iodine ($ZrI_{0.18}$) seems to be cracked and brittle.

ACKNOWLEDGMENT

Financial support for this research was provided by the U.S. Energy and Research Administration, Division of Physical Research under Contract No. E(04-3)-1339.

REFERENCES

- (1) JANAF Thermochemical Tables, The Dow Chemical Co., Midland Michigan, revised December 13, 1976.
- (2) D. Cubicciotti and K. H. Lau, "Thermodynamics of Vaporization of Zirconium Tetraiodide," paper submitted to J. Electrochem. Soc.
- (3) O. Rahlfs and W. Fischer, Z. Anorg. Allgem. Chem. **211**, 349 (1933).
- (4) W. Weltner, Jr. Abstract No. 386, This Symposium. Also personal communication.
- (5) D. L. Hildenbrand, D. Cubicciotti, P. Kleinschmidt, "Thermochemical Studies of the Gaseous Zirconium Iodides," in preparation.

- (6) C. E. Moore, "Atomic Energy Levels," NSRDS-NBS-35 Vol. II. National Bureau of Standards, Washington, D.C., 1971.
- (7) R. S. Ackermann and G. Rauh, J. Chem. Thermo., 4, 521 (1972).
- (8) D. Cubicciotti, J. Phys. Chem. 65, 1058 (1961).
- (9) D. D. Wagman et al., National Bureau of Standards Technical Note 270, U.S. Government Printing Office, Washington, D.C., 1968-73.
- (10) Z. M. Shapiro, "Iodide-Decomposition Process for Production of Zirconium," Chapter 5 in B. Lustman and F. Kerze, Metallurgy of Zirconium, McGraw Hill Book Co., N. Y., 1955.
- (11) H. Doring and K. Moliere, Z. Elektrochem., 56, 403 (1952).
- (12) J. D. Fast, Z. Anorg. Allgem. Chem. 239, 145 (1938).
- (13) R.A.J. Shelton, Inst. Min. Met. Trans. 77, C113 (1968).
- (14) F. R. Sale and R.A.J. Shelton, J. Less Common Metals. 9, 64 (1964); D. B. Copley and R.A.J. Shelton, *ibid*, 20, 359 (1970); A. S. Normanton and R.A.J. Shelton, *ibid*, 32, 111 (1973).
- (15) R. L. Daake and J. D. Corbett, "The Synthesis and Nonstoichiometry of the Zirconium Trihalides," submitted to Inorg. Chem; also Corbett et al, This symposium, Abstract No. 383.
- (16) R.A.J. Shelton, personal communication.
- (17) B. Cox and J. C. Wood, "Iodine Induced Cracking of Zircaloy Fuel Cladding - A Review" in C. S. Tedman, Jr., Ed., "Corrosion Problems in Energy Conversion and Generation," The Electrochem. Soc. Princeton, New Jersey, 1974.
- (18) J. C. Wood, J. Nucl. Mat. 45, 105 (1972/73).

Table 5

EQUATIONS FOR CALCULATION OF IONIC ENERGIES OF GASEOUS ZIRCONIUM IODIDES

$$U = -12.32 \frac{e^2}{r} \left(1 - \frac{1}{n}\right) - 16.48 \alpha \frac{e^2}{r^4} \left(1 - \frac{4}{n}\right)$$

$$U = 1845 \text{ kcal/mol}; \Delta H = 1831 \text{ kcal/mol}$$

$$U = -7.27 \frac{e^2}{r} \left(1 - \frac{1}{n}\right) - 8.17 \alpha \frac{e^2}{r^4} \left(1 - \frac{4}{n}\right)$$

$$U = 1047 \text{ kcal/mol}; \Delta H = 1030 \text{ kcal/mol}$$

$$U = -3.5 \frac{e^2}{r} \left(1 - \frac{1}{n}\right) - 3.06 \alpha \frac{e^2}{r^4} \left(1 - \frac{4}{n}\right)$$

$$U = 480 \text{ kcal/mol}; \Delta H = 480 \text{ kcal/mol}$$

$$U = - \frac{e^2}{r} \left(1 - \frac{1}{n}\right) - \frac{e^2}{2r^4} \beta \left(1 - \frac{4}{n}\right)$$

$$U = 145 \text{ kcal/mol}; \Delta H = 161 \text{ kcal/mol}$$

Values used for parameters in calculations

$$r = 2.66 \times 10^{-8} \text{ cm}$$

$$n = 11 \text{ (Reference 8)}$$

$$\alpha = 6.42 \cdot 10^{-24} \text{ cm}^3 \text{ (Reference 8)}$$

$$\beta = \alpha + 9 \times 10^{-24} \text{ cm}^3 \text{ (estimate for polarizability of } \text{Zr}^{+1})$$

Enthalpies of formation of gaseous ions taken from Reference 9.

Table 1

APPEARANCE POTENTIALS OF IONS PRODUCED FROM VARIOUS
NEUTRAL PRECURSORS

Ion Formed	Neutral Precursor	Appearance Potential, eV*
ZrI_4^+	ZrI_4	9.3 (700 K)
ZrI_3^+	ZrI_3	7.5 (1200 K)
	ZrI_4	10.5 (700 K)
ZrI_2^+	ZrI_3	10.1 (1200 K)
	ZrI_4	14.0 (700 K)
ZrI^+	ZrI	7.0 (2200 K)
	ZrI_2	10 (1500 K)
	ZrI_3	13.5 (1200 K)
	ZrI_4	17.3 (700 K)
Zr^+	Zr	6.5 (2200 K)
	ZrI_3	16.0 (1200 K)
	ZrI_4	21.0 (700 K)
I^+	I	10.5 (1000 K)

*Estimated uncertainties ~ 0.3 eV

Cell temperatures at which the listed threshold
were observed are given in parentheses.

Table 2

MEASURED EQUILIBRIA AND ENTHALPY CHANGES

Range, K		ΔH_{298}° kcal/mole
1124-1394	(1) $1/4 \text{ Zr(s)} + 3/4 \text{ ZrI}_4(\text{g}) = \text{ZrI}_3(\text{g})$	32.6 ± 1.5
1158-1394	(2) $\text{ZrI}_4(\text{g}) = \text{ZrI}_3(\text{g}) + \text{I}(\text{g})$	79.8 ± 1.5
1431-1478	(3) $\text{ZrI}_2(\text{g}) + \text{ZrI}_4(\text{g}) = 2\text{ZrI}_3(\text{g})$	-12.5 ± 3
2222-2434	(4) $\text{ZrI}(\text{g}) = \text{Zr}(\text{g}) + \text{I}(\text{g})$	72.6 ± 2

Table 3

ENTHALPIES OF FORMATION OF GASEOUS ZIRCONIUM IODIDES

	ΔH_{298}° Enthalpy of Formation kcal/mol
ZrI_4	-84.9 ± 1.5 (-86.6)*
ZrI_3	-30.8 ± 2 (-53)
ZrI_2	35.8 ± 3 (-16)
ZrI	96.3 ± 3 (141.3)

*Values in parentheses are from the JANAF Tables.

Table 4

BOND DISSOCIATION REACTIONS AND ENERGIES

	Bond ^b Dissociation Energy kcal/mole
$\text{ZrI}_4 \rightarrow \text{ZrI}_3(4d^1)^a + \text{I}$	79.6 ± 3.5
$\text{ZrI}_3 \rightarrow \text{ZrI}_2(4d^2) + \text{I}$	92.1 ± 5
$\text{ZrI}_2 \rightarrow \text{ZrI}(4d^2 \ 5s^1) + \text{I}$	86 ± 6
$\text{ZrI} \rightarrow \text{Zr}(4d^2 \ 5s^2) + \text{I}$	$72.6^c \pm 4$
$\rightarrow \text{Zr}(4d^3 \ 5s^1) + \text{I}$	$86.5^d \pm 4$

^aSymbols in parentheses are electronic states of the uncombined electrons. The states are assumed to be the same as those of the free gaseous zirconium ions given in Moore (6).

^bBased on the enthalpy of formation of gaseous I from JANAF Tables, namely 25.5 kcal/mol.

^cBased on the enthalpy of formation of 143.4 ± 1.3 kcal/mol from Reference 7.

^dBased on (c) and the energy of the electronic state above the ground state, given in Reference 6.

FIGURE 1 - Partial Pressures of Zr-I Species in Equilibrium with Zr(s) Calculated from Literature Estimates (Total equivalent iodine pressure = $\sum x p(\text{ZrI}_x) + Y p(\text{I}_2) = 10^{-4}$ atm)

FIGURE 2 - Partial Pressures of Zr-I Species in Equilibrium with Zr(s) at 10^{-4} atm of Iodine, from Present Data

FIGURE 3 - Partial Pressures of Zr-I Species in Equilibrium with Zr(s) at 1 atm of Iodine, from Present Data

FIGURE 4 - Partial Pressures of Zr-I Species in Equilibrium with Zr(s) at 10^{-5} atm of Iodine from Present Data

FIGURE 5 - Solid Zr-I Phases Reported by Various Workers. Regions of Homogeneous Solid Solution are Indicated by a Circled 1 and Two Phase Regions by Horizontal Lines

FIGURE 6 - Scanning Electron Microscope Photo of a Zircaloy Surface After Exposure to Iodine. (Width of Photo Represents $100 \mu\text{m}$.) Phases were Analyzed by X-ray Fluorescence. The Gravel-like Material on Most of the Surface was $\text{ZrI}_{1.0}$; the Pock-marked Crystals $\text{ZrI}_{1.7}$; the Smooth Needles ZrI_4 ; and the Layered Crystals $\text{ZrI}_{0.18}$

International Atomic Energy Agency

IWGFT/3

Appendix C

INTERNATIONAL WORKING GROUP ON FUEL PERFORMANCE
AND TECHNOLOGY FOR WATER REACTORS

**Specialists' Meeting
on
INTERNAL FUEL ROD CHEMISTRY**

**Erlangen, Federal Republic of Germany
23 – 25 January 1979**

THE CHEMISTRY OF THE ZIRCONIUM-IODINE SYSTEM

By

Daniel Cubicciotti

SRI INTERNATIONAL

Menlo Park, California 94025 USA

To be presented at

IAEA Specialists Meeting on

Internal Fuel Rod Chemistry

January 23-25, 1979, Erlangen, Germany

ABSTRACT

The enthalpies of formation of gaseous ZrI_3 , ZrI_2 , ZrI were determined from mass spectrometer measurements. Calculations of the partial pressures of the gaseous species in equilibrium with zirconium metal showed that ZrI_4 was the major gaseous species under conditions of importance in LWR fuel rods. Measurements of the pressure of ZrI_4 over the solid iodides have been used to determine the composition of stable solids. Ranges of homogeneity corresponding to a tetra, tri, di, mono, and possibly semiodide were observed. SEM studies of the formation of surface layers of iodides on zirconium provided some insight into the reaction mechanism. The relationship of these results to the stress corrosion cracking of zirconium alloys is discussed.

Zirconium and its alloys are subject to stress corrosion cracking induced by iodine (1). The fractography of cracks formed in iodine is very similar to that observed in the PCI failure of Zircaloy clad fuel rods (2). We believe that fission product iodine is the aggressive agent in PCI failures (2) and thus it is important to understand the chemistry of the zirconium-iodine system to help clarify the SCC mechanism. Our research on the chemistry of the system is funded by the USDOE and parallels our research related to the conditions for SCC of Zircaloy funded by EPRI (3).

Gaseous Iodide - The enthalpies of formation in the literature for zirconium iodides, except ZrI_4 , are generally incorrect. They are all based either on estimates or dubious interpretations of experimental results. We have recently (4) used a mass spectrometer method to measure the partial pressures of the gaseous iodides in equilibrium with zirconium metal. From those results the enthalpies of formation of gaseous ZrI_3 , ZrI_2 , and ZrI were derived. The details of the methods used and the results obtained have been reported in the literature (4). Table 1 summarizes the thermodynamic data and Figure 1 gives the partial pressures of the gases in equilibrium with zirconium metal at two different pressures of total iodine-containing species [i.e., $P(\text{total I})$].

For temperatures typical of Zircaloy cladding inner surfaces in LWR operation (~ 650 K) the only important gaseous species containing Zr is ZrI_4 . As $P(\text{total I})$ decreases the lower iodides become more important relative to ZrI_4 ; however at 650 K the gases dissociate to iodine before the lower iodides become more important than ZrI_4 . Therefore any mechanism for iodine induced SCC of Zircaloy that involves transport of Zr must invoke ZrI_4 primarily.

Solid Iodides - We are currently studying the thermodynamics of the solid zirconium iodides by measurements of vapor pressures. We have demonstrated, above, that at equilibrium with Zr metal the pressures of ZrI_4 are much larger than those of the lower iodides (ZrI_3 , ZrI_2 , ZrI). Thermodynamic considerations lead to the conclusion that the vapor in equilibrium with any solid iodides must be even richer in ZrI_4 than in lower iodides. Therefore the vapor in equilibrium with any solid iodides is essentially ZrI_4 . In our investigations the partial pressures of ZrI_4 in equilibrium with the solid iodides are measured by a torsion-effusion technique. At the same time the cell is suspended from a microbalance so that the amount of ZrI_4 evaporated is known, and from that the composition of the solid remaining in the cell can be determined. The method has been described in our work in the thermodynamics of vaporization of ZrI_4 (5).

The vaporization of gaseous ZrI_4 from the solid iodide must be interpreted on the basis of the phase rule. The gas is always ZrI_4 ; therefore for a single condensed phase, the system is bivariant and the pressure depends on temperature and composition of the solid. For two condensed phases the system is univariant and the vaporization reaction can be generalized as follows:

Therefore as ZrI_4 is evaporated from a solid that is initially ZrI_{4-x} , the composition of the solid changes and x becomes larger, eventually reaching 4. For a fixed temperature, the pressure of ZrI_4 is constant when two solids are in equilibrium and decreases in one solid phase regions. Shelton and coworkers have used this method for part of the Zr-I system (6). We have studied other regions of the system (7) and have combined those results together with the composition studies of Corbett et al. (8). Our interpretation of the vaporization results is summarized as follows. There are regions of one phase homogeneous solid solution, namely,

$\text{ZrI}_{4+\delta}$ to $\text{ZrI}_{4-\gamma}$ "tetraiodide"

(δ and γ are as yet unknown)

$\text{ZrI}_{3.4}$ to $\text{ZrI}_{2.8}$ "triiodide"

$\text{ZrI}_{2.1}$ to $\text{ZrI}_{1.9}$	"diiodide"
$\text{ZrI}_{1.3}$ to $\text{ZrI}_{1.1}$	"moniodide"
$\text{ZrI}_{0.5}^{(?)}$ to $\text{ZrI}_{0.2}^{(?)}$	"semiiodide"

The composition limits are probably correct to ± 0.1 . The information about these phases is less certain the smaller the iodine content, and in fact, we are not yet sure that the semiiodide exists.

Between the homogeneous solids are regions in which two solid phases are in equilibrium. The situation is represented graphically in Figure 2, which presents an isothermal cut of the pressure-composition diagram. The far right side of the diagram is still uncertain. A pressure-temperature diagram is given in Figure 3. The lines represent the pressures of ZrI_4 in the univariant regions, i.e., with two solid phases present. They correspond to the pressures of gaseous ZrI_4 for the following equilibria

The phase $\text{ZrI}_{0.5}$ and $\text{ZrI}_{0.2}$, i.e. the "semiodide" phase, has been identified in scanning electron microscope pictures but we are not sure that the interpretation of the vapor pressures in that region, shown in Figure 3, is correct.

Kinetics of Reaction - We also have made some observations about the kinetics of the reaction. The reaction of iodine vapor with clean zirconium metal is rapid and forms a protective layer of solid iodides on the surface. We have studied the somewhat milder reaction of gaseous ZrI_4 with zirconium surfaces. Samples of Zr sheet and ZrI_4 solid were sealed into evacuated glass bulbs whose ends were heated to different temperatures for fixed periods of time. The bulbs were opened in a dry box and the metal sample transferred under dry inert atmosphere to a scanning electron microscope for surface examination.

The first reaction products formed on the surface are the isolated crystals of semiodide shown in Figure 4. The surface of the metal between the crystals has a thin layer of iodide. For longer exposure times, the crystals increase in size and also in stoichiometry, reaching a composition of about the moniodide. When the moniodide crystals have grown so large that they cover the surface, they become covered by diiodide. Figure 5 shows a surface covered by diiodide of varying stoichiometry. We presume that the regions of different sizes of crystal correspond to various grains in the substrate metal that have orientations of

differing reactivity exposed to the gas. Figure 6 shows the cross section of a relatively thick surface film of iodides. The film has a layered structure, the large crystals on the top are triiodide, the compact columnar layer is monoiodide and there is a thin layer of diiodide between the two layers. The diiodide is not readily discerned in the figure but can be identified under higher magnification.

Relation to SCC - Peehs et al. (9) have determined the smallest amount of iodine needed to cause SCC of Zircaloy. Because the mechanism of SCC is not known, it was not certain whether that minimum amount of iodine acted in the vapor phase (as gaseous ZrI_4) or on the surface (as a layer of solid iodides). The minimum amount of iodine corresponded to 1×10^{-6} gm/cm² of Zircaloy surface if it was a surface layer. Those authors used the available (but incorrect) thermodynamic information to conclude that the onset of SCC occurred when the amount of iodine was just sufficient to form a surface layer.

The cross shown in Figure 3 indicates the pressures of ZrI_4 that would have resulted from the minimum amount of iodine in the tests of Peehs et al. if it were all gaseous (as ZrI_4). It can be seen that solid iodides form at much lower pressures (more than 10^{-5} lower). Therefore the conclusion of Peehs et al that the iodide was solid and not gaseous was correct; however the pressure does not correspond to the lowest iodide. In other observations they showed that a solid surface iodide on the

Zircaloy must form to produce SCC. Therefore the proper form for the effect of concentration of iodine on SCC is the surface concentration, and the minimum value is about 10^{-6} gm/cm² from their work.

For an LWR fuel rod, fission product cesium is available as vapor in the fuel-clad gap. Cesium is very reactive toward iodine; therefore on a thermodynamic basis one expects all the iodine in an irradiated fuel rod to be combined as CsI, which does not cause SCC of itself. We have shown that crystals of CsI do form on the innersurfaces of LWR fuel rod cladding under certain conditions (10). We have also shown that gamma radiolysis can release iodine from CsI (11). Thus we believe that crystals of CsI deposited on the inner cladding surface act as sources of iodine which is released by radiolysis from the CsI. The iodine reacts with the Zircaloy surface immediately beneath the deposit in areas where the cesium vapor cannot easily reach. The amounts of iodine that could be transferred from a CsI deposit to the cladding surface in a fuel rod are estimated (2) to be substantially greater than the minimum values measured in laboratory tests. A schematic representation of the transfer process is shown in Figure 7.

ACKNOWLEDGMENTS

This research was supported by the Division of Basic Energy Science of the U.S. Department of Energy with Dr. Robert P Eppele as technical monitor. The author is grateful for assistance in this work to Drs. D. L. Hildenbrand, R. L. Jones, P. Kleinschmidt, D. Knittel, K. Lau, and A. Scott of SRI and H. Ocken and J.T.A. Roberts of EPRI.

REFERENCES

1. B. Cox and J. C. Wood, "Iodine Induced Cracking of Zircaloy Fuel Cladding--A Review," in Corrosion Problems in Energy Conversion Generation; ed. C. S. Tedmon, Jr., The Electrochemical Society, Princeton, N. J. 1974.
2. J.T.A. Roberts, et al., "An SCC Model for Pellet-Cladding Interaction Failures in LWR Fuel Rods," in Fourth International Conference on on Zirconium in the Nuclear Industry (1978), to be published by ASTM, Philadelphia, Pa.
3. D. Cubicciotti and R. L. Jones, "EPRI-NASA Cooperative Project on Stress Corrosion Cracking in Zircalloys," Final Report, EPRI-NP 717, Electric Power Research Institute, Palo Alto, California 1978.
4. P. D. Kleinschmidt, D. Cubicciotti, D. L. Hildenbrand, J. Electrochem. Soc., 125, 1543 (1978).
5. D. Cubicciotti, K. H. Lau, M. J. Ferrante, J. Electrochem. Soc., 125, 972 (1978).
6. M. A. Bhatti, D. B. Copley, R.A.J. Shelton, J. Less Common Metals 55, 293 (1977).
7. D. Cubicciotti, K. H. Lau, "Thermodynamics of Vaporization of ZrI_4 from Substoichiometric Solid Zirconium Iodides," J. Electrochem. Soc., to be published.

8. J. D. Corbett, et al., J. Am. Chem. Soc. 100, 652 (1978).
9. M. Peehs, H. Stehle, E. Steinberg, "Out-of-Pile Testing of Iodine Stress Corrosion Cracking in Zircaloy Tubing Under the Aspect of the PCI-Phenomenon," in Fourth International Conference on Zirconium in the Nuclear Industry (1978), to be published by ASTM, Philadelphia, Pa.
10. D. Cubicciotti and J. E. Sanecki, J. Nuclear Mat. 78, 96 (1978).
11. D. Cubicciotti and J. H. Davies, Nucl. Sci. Eng. 60, 314 (1976).

Table 1

THERMODYNAMIC CONSTANTS FOR GASEOUS ZIRCONIUM IODIDES
(From Reference 4)

Gaseous Species	Standard Enthalpy of Formation 298 K kJ/mol	Standard Tempered Gibbs Energy, Relative to 298,* J/mol	
		500 K	1000 K
ZrI ₄	-355	459	501
ZrI ₃	-129	410	442
ZrI ₂	+136	354	378
ZrI	+403	280	296

*I.e. - $\frac{\Delta G^\circ(T) - \Delta H_{298}}{T}$

FIGURE CAPTIONS

- Figure 1 Partial Pressures of Gases in Equilibrium with Solid Zirconium
(a) For $P(\text{total I}) = 10^{-4}$ atm
(b) For $P(\text{total I}) = 10^{-8}$ atm
($P(\text{total I})$ = sum of pressures of iodine species expressed as atomic iodine)
- Figure 2 Pressure of ZrI_4 as a function of composition of Solid Zr-I Phases at 650 K. Dashed lines indicate estimated portions.
- Figure 3 Pressure of ZrI_4 as a Function of Reciprocal Temperature. The cross indicates the minimum iodine for SCC observed by Peehs et al. Formulas indicate compositions of solids at two phase boundaries.
- Figure 4 SEM Photograph of surface of Zirconium Exposed at 625 K to 100 Pa of gaseous ZrI_4 for 15 minutes. Analysis showed the light gray crystals had a ratio of I to Zr of about 0.5. The darker gray regions were Zr with a trace (surface layer) of I. (Width of Photograph = 20 μm .)
- Figure 5 SEM Photograph of Surface of Zirconium Exposed at 625 K to 100 Pa of gaseous ZrI_4 for 24 hours. Analysis of the darker gray crystals showed a ratio of I to Zr of 1.6 to 1.8 while for the light crystals the ratio was 2.3. (Width of Photograph = 20 μm .)
- Figure 6 SEM Photograph of the Cross Section of a Fractured Surface Layer of Iodides Formed on Zirconium Exposed at 775 K to 40 k Pa of Gaseous ZrI_4 for 24 Hours. Analysis of the crystals on top of the layer showed I to Zr of: 2.8; the columnar layer of crystals: 1.0 and a thin intermediate layer of 1.8. The Zirconium surface in the foreground had a trace of iodine. (Width of Photograph = 50 μm .)
- Figure 7 Schematic Representation of the Thermodynamically Unfavorable Transfer of Iodine from CsI to Form Zirconium Iodides on Cladding Inner Surfaces. Iodine is released from the CsI by radiolysis in regions beneath the deposits of fission products where Cs vapor cannot readily arrive. The Iodine is thus available to react with the Zr and result in SCC.

SA-5780-5

(a) For $P(\text{total I}) = 10^{-4}$ atm

SA-5780-7

(b) For $P(\text{total I}) = 10^{-8}$ atm

Figure 1 Partial Pressures of Gases in Equilibrium with Solid Zirconium
($P(\text{total I})$ = sum of pressures of iodine species expressed as atomic iodine)

Figure 2 Pressure of ZrI_4 as a function of composition of Solid Zr-I Phases at 650 K. Dashed lines indicate estimated portions.

TA-350543-84

Figure 3 Pressure of ZrI_4 as a Function of Reciprocal Temperature. The cross indicates the minimum iodine for SCC observed by Peehs et al. Formulas indicate compositions of solids at two phase boundaries.

Figure 4 SEM Photograph of surface of Zirconium Exposed at 625 K to 100 Pa of gaseous ZrI_4 for 15 minutes. Analysis showed the light gray crystals had a ratio of I to Zr of about 0.5. The darker gray regions were Zr with a trace (surface layer) of I. (Width of Photograph = 20 μm .)

Figure 5 SEM Photograph of Surface of Zirconium Exposed at 625 K to 100 Pa of gaseous ZrI_4 for 24 hours. Analysis of the darker gray crystals showed a ratio of I to Zr of 1.6 to 1.8 while for the light crystals the ratio was 2.3. (Width of Photograph = 20 μm .)

Figure 6 SEM Photograph of the Cross Section of a Fractured Surface Layer of Iodides Formed on Zirconium Exposed at 775 K to 40 k Pa of Gaseous ZrI_4 for 24 Hours. Analysis of the crystals on top of the layer showed I to Zr of: 2.8; the columnar layer of crystals: 1.0 and a thin intermediate layer of 1.8. The Zirconium surface in the foreground had a trace of iodine. (Width of Photograph = 50 μm .)

TA-350543-85

Figure 7 Schematic Representation of the Thermodynamically Unfavorable Transfer of Iodine from CsI to Form Zirconium Iodides on Cladding Inner Surfaces. Iodine is released from the CsI by radiolysis in regions beneath the deposits of fission products where Cs vapor cannot readily arrive. The Iodine is thus available to react with the Zr and result in SCC.

Appendix D

THERMODYNAMICS OF VAPORIZATION OF ZrI_4 IN THE UNIVARIANT
REGION: ZIRCONIUM MONOIODIDE/ZIRCONIUM

By

Daniel Cubicciotti and K. H. Lau

SRI International
Menlo Park, California 94025

ABSTRACT

The pressures of gaseous ZrI_4 over solid zirconium iodides in the composition range ZrI to Zr were measured by a torsion-effusion method. A univariant region was observed between solids of composition $\text{ZrI}_{1.05}$ and Zr for which the pressure of gaseous ZrI_4 was represented by the equation:

$$\text{Log}_{10} P(\text{atm}) = 12.83 - 13,200/T \quad .$$

These results extend literature information on the thermodynamics of vaporization in the ZrI_4/Zr region of the Zr-I system.

INTRODUCTION

The chemistry of the zirconium-iodine system is intimately involved in the mechanism of iodine-induced stress corrosion cracking of zirconium alloys.^{1,2} We have been investigating the thermodynamics to improve understanding of the chemistry of the system. The thermodynamic properties of the gaseous zirconium iodides are reported in Reference 3. We have studied the vaporization of gaseous ZrI_4 from the solids to evaluate the thermodynamic properties of the solid phases. The vapor pressure of pure, solid ZrI_4 is given in Reference 4.

In a recent paper,⁵ the partial pressures of gaseous ZrI_4 in equilibrium with substoichiometric solid zirconium iodides in the composition range $\text{ZrI}_{2.4}$ to $\text{ZrI}_{1.0}$ were determined by the torsion-effusion method. This technique requires no knowledge of vapor composition to evaluate total vapor pressure. Simultaneous mass loss and effusion rate measurements confirmed that the vapor contained only gaseous ZrI_4 , and the measurements gave average molecular weight values within experimental error of the value of ZrI_4 gas. A univariant region was found between the solids $\text{ZrI}_{1.9}$ and $\text{ZrI}_{1.3}$, and the equilibrium pressures of gaseous ZrI_4 were derived. Between $\text{ZrI}_{1.3}$ and $\text{ZrI}_{1.0}$ the vapor pressure decreased as effusion proceeded at constant temperature, indicating that a single phase solid solution region existed in this range.

The part of the zirconium-iodine system most relevant to the stress corrosion cracking problem is the region that includes zirconium metal. In this paper we report the vaporization of ZrI_4 from the two-solid-phase region that involves zirconium metal and the lowest iodide, approximately ZrI .

The principle of the method we used is described in Reference 5. A sample of solid zirconium iodide (of composition approximately $\text{ZrI}_{1.2}$) was heated in a torsion-effusion gravimetric system so that gaseous ZrI_4

was released. The pressure of the gas was measured from the torque of the cell. The composition of the solid was monitored through its weight change. As ZrI_4 evaporated, the average composition of the residual solid changed, becoming richer in zirconium. The results are given below.

Experimental Materials

The $\text{ZrI}_{1.2}$ samples loaded in the graphite effusion cells were prepared as follows: The starting material was $\text{ZrI}_{2.4}$ prepared as described earlier.⁵ A weighed amount of $\text{ZrI}_{2.4}$ was loaded in a graphite crucible and sealed under high vacuum into a 20-cm-long by 1.6-cm-diameter fused silica tube. The tube was placed in a two-zone tilted furnace. The lower 8 cm of the tube containing the sample was heated to 425°C . The upper 4 cm was kept at 140°C so that ZrI_4 vaporized from the sample condensed there, thereby maintaining a ZrI_4 vapor pressure of about 2×10^{-7} atm. The tube was heated in this temperature gradient for three weeks and was then transferred to a dry box under an atmosphere of argon. The tube was cracked in the center and a lump of reddish brown ZrI_4 product was collected from the upper end and weighed to obtain an estimate of the composition of the solid residue. The sample in the graphite crucible was a black, granular material. Two samples were prepared; part of each was used for chemical and X-ray diffraction analysis. The rest was loaded into the effusion cells, one sample into cell A, the other into cell B. Titration with silver ion to an iodide electrode end point showed the composition of the starting material was $\text{ZrI}_{1.2} \pm 0.1$ for cell A and $\text{ZrI}_{1.1} \pm 0.1$ for cell B. These starting compositions were in good agreement with the total mass lost by the cells in the vaporization study, during which all the iodide was evaporated from the cell (see below). The X-ray powder diffraction pattern of the sample of cell A is given in Table 1.

Table 1

X-RAY POWDER PATTERN* of $\text{ZrI}_{1.2}$

$\frac{d}{\text{\AA}}$	I/I_1
8.6	25
4.32	30
3.84	35
3.62	35
3.48	10
3.31	100
3.02	5
2.91	5
2.88	5
2.77	3
2.70	5
2.58	25
2.44	50
2.26	50
2.17	60
2.04	5
1.94	3
1.92	3
1.89	5
1.82	20
1.73	10
1.66	15
1.61	10
1.53	5
1.48	10
1.44	10
1.39	5
1.37	5
1.30	25
1.27	5
1.26	5

*Obtained with a 2 inch diameter camera and $\text{CuK}\alpha$ radiation.

Vapor Pressure Measurement

Vapor pressures were measured by the torsion-effusion method. The apparatus, the sample loading procedures, and other details of this method were described in our earlier publications.^{4,5} Two series of vapor pressure measurements were made with graphite effusion cells labeled cell A (0.047-cm orifice diameter) and cell B (0.0803-cm orifice diameter). These are the same two cells used in our earlier work^{4,5} and described in detail there.³

RESULTS

The results of the measurements are listed in Table 2. The data are presented in the chronological order in which they were obtained. The pressure (column 2) was calculated from the measured angular displacement of the torsion effusion cell at each temperature. The molecular weight of the effusing gas (column 3) was calculated from the pressure and the rate of mass loss of the cell. The composition of the solid (column 4) was calculated from the initial sample weight and the total mass loss incurred by the sample, assuming the vapor lost was gaseous ZrI_4 . The last column of the table, $P_{\text{obs}}/P_{\text{calc}}$, gives the ratio of the measured pressure divided by the pressure calculated from one of the equations that represents the univariant region for the given cell, namely, Equations (1) or (2) below.

The molecular weights observed (column 3) were in the range 579 to 637, which is within the experimental error of the method for ZrI_4 gas--namely, 599. Vapor in equilibrium with zirconium metal under these conditions can be shown to contain essentially ZrI_4 , with only traces of lower valent gas.³ Thus the gas was presumed to be pure ZrI_4 in all these measurements.

The pressures observed for cell A over the range of composition of the solid in the cell of $\text{ZrI}_{1.07}$ to $\text{ZrI}_{0.57}$ could be represented, within $\pm 3\%$, by a single equation independent of composition, as follows:

Table 2

RESULTS OF TORSION-EFFUSION, MASS LOSS MEASUREMENTS
IN THE $ZrI_{1.2}$ to Zr REGION

Temperature K	Pressure of ZrI_x atm $\times 10^6$	Molecular Weight of gas	Composition of Solid, X of ZrI_x	$\frac{P_{obs}}{P_{calc}}$	Temperature K	Pressure of ZrI_x atm $\times 10^6$	Molecular Weight of gas	Composition of Solid, X of ZrI_x	$\frac{P_{obs}}{P_{calc}}$
Cell A (0.5 mm diameter orifices)					Cell B (0.8 mm diameter orifices)				
736.2	2.12		1.14	0.67	726.4	0.68		1.05	0.99
760.7	9.10		1.12	0.77	759.1	3.94	589	0.98	0.97
769.4	15.63	637	1.10	0.85	740.1	1.48			1.01
780.5	29.12	628	1.08	0.93	754.1	3.06			0.98
					749.3	2.34			0.97
771.6	19.42		1.07	0.95	738.8	1.31			0.96
750.9	6.92	609	1.06	0.99	743.2	1.67			0.96
755.8	8.81			0.97	765.7	5.62			
763.9	13.47		0.97		762.3	4.72			0.99
772.8	21.35				769.7	7.10			
754.0	8.17		1.04	0.98	767.3	6.24			1.02
770.5	18.89				755.4	3.37			
768.2	16.75				759.7	4.24			
778.7	29.43			1.00	736.2	1.18			
777.3	27.56	618			747.1	2.14			
753.8	8.21				738.4	1.32			0.99
756.6	9.57				742.3	1.63			
769.8	18.82				756.8	3.60			
768.3	17.42		0.98	1.00	754.1	3.14			
750.2	6.92	599		1.02	763.0	5.04			
758.0	10.31				760.3	4.41			
772.1	21.53			1.02	751.7	2.82	579		1.03
770.2	19.32				765.2	5.68	585		
777.9	29.08				771.8	8.05			
755.1	9.13	601			768.1	6.64		0.92	1.03
749.4	6.79				733.1	1.02			
751.3	7.06			0.99	744.4	1.87			
771.0	20.69				736.4	1.22			
749.2	6.62				740.2	1.48			
752.1	7.58				755.5	3.38			
763.3	13.58			1.01	752.9	2.91	591		
759.9	11.41				763.2	5.05			1.01
775.7	25.81				749.6	2.45			
774.7	24.71				746.4	2.07			
777.6	28.57				741.7	1.62			
751.0	7.19			1.02	766.2	5.69	587.4		
768.0	17.21				764.9	5.31			
770.5	19.59		0.90	1.00	771.4	7.53			
747.2	5.77				753.0	2.89	584	0.85	0.99
754.0	8.26			1.00	750.0	2.45			
750.7	6.83				738.8	1.38			
775.7	25.31				757.2	3.53			
775.0	24.39				754.1	2.99			
778.1	28.55				738.8	1.35			0.99
771.1	19.79			0.99	742.7	1.64			
753.5	7.94				767.7	5.93		0.77	0.95
759.7	10.97				764.9	5.11		0.65	
758.9	10.37			0.84					
749.2	6.32			0.99	774.5	6.44		0.57	0.73
754.8	8.40				773.4	5.63	579		
752.9	7.51				773.5	4.28	577	0.33	0.51
775.5	24.51				773.5	1.75		0.07	0.21
774.0	22.59				773.5	0.36		0.03	0.04
778.6	20.65		0.80	0.98					
775.6	24.45		0.57	0.97					
775.5	22.83		0.56	0.91					
775.7	21.80		0.46	0.86					
776.7	19.31		0.28	0.72					
776.0	9.98		0.18	0.39					
773.9	5.13		0.15	0.22					
869.7	5.45	604	0.08	0.003					
897.4	10.56	580	0.04						
928.8	10.16		0.01	0.001					

$$\log_{10} P(\text{atm}) = (12.26 \pm 0.10) - (13080 \pm 80)/T \quad (745 \text{ to } 980 \text{ K}) \quad (1)$$

The pressures observed for cell B over the composition range $\text{ZrI}_{1.05}$ to $\text{ZrI}_{0.65}$ could also be represented by an equation independent of composition, as follows:

$$\log_{10} P(\text{atm}) = (11.75 \pm 0.11) - (13010 \pm 90)/T \quad (730 \text{ to } 722 \text{ K}) \quad (2)$$

The uncertainty given in each equation is a standard deviation derived in a least squares treatment. The data are shown graphically in Figure 1.

As part of our investigation⁵ of ZrI_4 pressure in the solid composition range $\text{ZrI}_{2.4}$ to $\text{ZrI}_{1.3}$ we made some preliminary measurements at lower stoichiometries. Those measurements showed evidence for univariant behavior at compositions below about ZrI . Because of the small amount of sample remaining in the cells at compositions below ZrI (since the initial composition was $\text{ZrI}_{2.4}$), we were not sure of the reliability of the results and did not publish them at that time. The pressures observed in those experiments were found to be in good accord with the present data measured on samples of initial composition $\text{ZrI}_{1.2}$. The values found as part of the Reference 5 measurements were as follows for cell A:

$$\log_{10} P(\text{atm}) = (11.92 \pm 0.4) - (12850 \pm 290)/T \quad (740 \text{ to } 780 \text{ K}) \quad (3)$$

These values in cell A were observed over the range of compositions of $\text{ZrI}_{0.97}$ to $\text{ZrI}_{0.89}$. At lower stoichiometries the measured pressures were smaller. For cell B the results were represented by:

$$\log_{10} P(\text{atm}) = (11.38 \pm 0.2) - (12750 \pm 130)/T \quad (740 \text{ to } 780 \text{ K}) \quad (4)$$

These values in cell B were observed over the composition range $\text{ZrI}_{0.96}$ to $\text{ZrI}_{0.53}$. At lower stoichiometries the pressures were smaller than Equation (4). These results are shown in Figure 1 as dashed lines.

The values of Equation (3) (cell A) are about 10% smaller than Equation (1), and those of Equation (4) (cell B) are about 6% smaller than Equation (2). The data represented by Equations (3) and (4) were considered to be less accurate than those of Equations (1) and (2) and so were not used further.

SA-5780-26

FIGURE 1 VAPOR PRESSURES OF ZrI_4 IN THE UNIVARIANT REGION OF THE SYSTEM BETWEEN ZrI AND Zr

Data points represent values from Table 2 and solid lines are least squares equations (1) and (2). Dashed lines are results obtained earlier and work represented by equations (3) and (4). Dot-dash lines give equilibrium pressures obtained by extrapolation to zero orifice area.

The differences between the values obtained in cell A and cell B were assumed to be due to the usual influence of effusion orifice size on apparent calculated pressure. The effect of orifice size on the measured pressure was treated by the Whitman-Motzfeld method;⁴ which indicates that the reciprocal of measured pressure is expected to vary linearly with effective orifice area. For the cells used in the present work the effective orifice areas were 0.125 mm² for cell A and 0.478 mm² for cell B. The equilibrium pressures derived by extrapolation of the reciprocals of the pressures measured in cells A and B versus their effective orifice areas are represented by the dot-dash line in Figure 1. An equation representing those equilibrium pressures for the univariant composition region of the present work is

$$\log_{10} P_{eq}(\text{atm}) = (12.83 \pm 0.1) - (13200 \pm 100)/T \quad (720 \text{ to } 790 \text{ K}) \quad (5)$$

When the composition of the solid dropped below ZrI_{0.57} in cell A and ZrI_{0.65} in cell B, the measured pressures fell below the values anticipated from equations (1) and (2), respectively. That effect can be noted from the values given in the last column of Table 2, which represents the ratios of the measured pressures (of ZrI₄) divided by the values calculated from Equation (1) or (2), respectively for cell A or B. The ratios are shown graphically as a function of composition in Figure 2. The solid remaining in cell A after the series of pressure measurements reported in Table 2 was analyzed and found to correspond to an I/Zr ratio of 0.003. An X-ray powder diffraction pattern of that material showed only lines corresponding to alpha zirconium.

The ratios in Figure 2 depart from unity in a fairly smooth fashion. We interpret this behavior to indicate that no new phase was being formed, and that the deviation from unity resulted from depletion of the samples in the cells. The fact that the cell B ratios fell off at lower I/Zr stoichiometries was in keeping with that interpretation.

To corroborate the above result, a sample of ZrI_{2.4} in a graphite crucible was heated for 45 days at 475°C in a sealed glass bulb with one end of the bulb maintained at about 50°C. During the heating period,

SA-5780-27

FIGURE 2 RATIO OF MEASURED PRESSURE TO VALUE CALCULATED FROM EQUATION (1) (FOR CELL A) OR EQUATION (2) (FOR CELL B) AS A FUNCTION OF COMPOSITION OF SOLID REMAINING IN CELL
Dots and crosses represent cell A and cell B data, respectively.

ZrI₄ vaporized from the sample and condensed in the cold end of the bulb. The sample remaining in the crucible was analyzed and found to be ZrI_{0.1}. An X-ray powder pattern of that material showed lines mainly corresponding to alpha zirconium. The remaining lines were the same as the X-ray pattern for ZrI given in Table 1, and the overall intensity was about one-tenth that of the alpha zirconium pattern. That result indicates that the equilibrium phases present for the overall composition ZrI_{0.1} were ZrI and alpha Zr.

The univariant region corresponding to the pressures given in Equation (3) was observed for I/Zr ratios as high as 1.05 and the discussion above gives evidence that it extended to pure zirconium. Therefore, the chemical reaction corresponding to the pressures of Equation (3) is:

The enthalpy change derived from Equation (5) for reaction (6) is 60.4 ± 0.5 kcal/mole.

Figure 3 indicates our assessment of the vaporization thermodynamics for the zirconium iodides; the assessment combines our earlier results with the present data. Zirconium tetraiodide is the predominant vapor species, and the partial pressure of ZrI₄ as a function of composition of the solid is shown in the upper curve. The horizontal segments of the curve correspond to univariant regions, that is, regions in which two solids exist in equilibrium with the vapor (ZrI₄). The nonhorizontal portions represent regions of solid solution that have approximately the stoichiometries of the tetraiodide, triiodide, diiodide, monoiodide, and the metal and are so indicated on the diagram. The enthalpies of vaporization per mole of ZrI₄ gas are presented in the lower curve of Figure 3. The enthalpies of vaporization became greater the smaller the I/Zr ratio of the solid, which indicates that the removal of ZrI₄ from the solid becomes energetically more difficult as the composition decreases in iodide.

SA-5780-28

FIGURE 3 THERMODYNAMICS OF VAPORIZATION AS A FUNCTION OF COMPOSITION IN THE Zr-I SYSTEM

Upper curve, pressure of ZrI₄ at 650 K; lower curve, enthalpies of vaporization reactions per mole of ZrI₄. Dashed lines indicate regions of estimated data.

ACKNOWLEDGMENTS

This research was supported by the Office of Basic Energy Science of the U.S. Department of Energy under Contract EY-76-S-03-1339. We are grateful to D. R. Knittel for some of the experimental work, to A. C. Scott for preparation of the samples, and to Eldon Farley for X-ray diffraction patterns.

REFERENCES

1. B. Cox and J. C. Wood in Corrosion Problems in Energy Conservation and Generation, C. S. Tedman Jr., ed., The Electrochemical Society, New York, 1974, p. 275.
2. J. H. Schemel and T. P. Papazoglou, eds., Zirconium in the Nuclear Industry, ASTM Special Technical Publication 681, (Am. Soc. Test Mat., Philadelphia, PA, pp. 229 to 321, 1979).
3. P. D. Kleinschmidt, D. Cubicciotti and D. L. Hildenbrand, J. Electrochem. Soc. 125, 972 (1978).
4. D. Cubicciotti, K. H. Lau, and M. J. Ferrante, J. Electrochem. Soc. 125, 972 (1978).
5. D. Cubicciotti and K. H. Lau, J. Electrochem. Soc. 126, 771 (1979).

Appendix G

THERMODYNAMIC PROPERTIES OF THE SOLID ZIRCONIUM IODIDES

By

Robert H. Lamoreaux and Daniel Cubicciotti

SRI International
Menlo Park, California 94025

ABSTRACT

The results of measurements of ZrI_4 pressures over solids of the zirconium-iodine system have been used to calculate Zr and ZrI_4 activities as functions of composition at 700 K. These activities were used, along with estimated heat capacities and entropies, to derive values of the activity of iodine and of the enthalpies of formation of solid stoichiometric ZrI , ZrI_2 , and ZrI_3 . Values of the enthalpy of formation are $\Delta H_{298}^\circ(\text{ZrI},s) = -34.0 \pm 2.5$ kcal/mole, $\Delta H_{298}^\circ(\text{ZrI}_2,s) = -66.4 \pm 2.5$ kcal/mole, $\Delta H_{298}^\circ(\text{ZrI}_3,s) = -93.6 \pm 4.5$ kcal/mole.

INTRODUCTION

The solid-state chemistry of the zirconium-iodine system, which must be known to understand the iodine-induced stress corrosion cracking of zirconium alloys, is complex and to a large extent undetermined. The earlier literature contains little thermodynamic information and is inconsistent about the compositions of solid phases. Recent torsion-effusion studies¹⁻³ of the pressure of ZrI_4 in equilibrium with solid zirconium iodides have established solid solution regions corresponding approximately to tetra-, tri-, di-, and monoiodide.

Vaporization measurements on solid zirconium iodides determine the pressure of ZrI_4 evolved according to the generalized equation:

Zirconium tetraiodide is the predominant gaseous metal iodide species in equilibrium with any condensed phase in the zirconium-iodine system below about 1000 K.²

The equilibrium behavior of the condensed phases must conform to the phase rule. A two-component system with a gas phase is univariant when there are two condensed phases (i.e., two immiscible solids) and bivariant when there is only one condensed phase (i.e., one solid solution of variable composition). The number of condensed phases and their compositions can be deduced from the behavior of the system during vaporization.

As ZrI_4 is removed by vaporization from a solid, substoichiometric solid or mixture of solids, the overall composition of the condensed phase becomes poorer in iodine. If the condensed phase consists of two solids, then the system is univariant and the equilibrium pressure of ZrI_4 depends only on the temperature of the system; in this case, removal of ZrI_4 by vaporization will not change the pressure, but will change only the amounts of the two solids present. If only one solid

phase is present (a solid solution), then the system is bivariant and the pressure of ZrI_4 depends on the composition of the solid solution as well as on the temperature; in this case, removal of ZrI_4 will cause the composition of the solid solution to change and the equilibrium pressure to decrease at constant temperature.

The composition limits of zirconium iodide solid phases are listed in Table I. These limits should vary somewhat with temperature, but the variation might be small, as found by Daake and Corbett⁴ for the triiodide. The tetraiodide has been characterized, except that there is no information about the range of composition over which it is stable. For this phase to be in equilibrium with triiodide, it must extend to $\text{ZrI}_{4-\gamma}$, since stoichiometric $\text{ZrI}_4(\text{s})$ vaporizes congruently.¹ The ZrI solid solution composition limits were established by X-ray and chemical analysis of equilibrated samples,⁴ whereas those of the ZrI_2 and ZrI phases were established by observation of one- and two-solid-phase vaporization behavior.^{2,3,5} Two-solid-phase behavior was observed³ between $\text{ZrI}_{1.05}$ and Zr . The two equilibrium solids in that region were determined from X-ray analysis of a sample of composition $\text{ZrI}_{0.1}$; which indicated that the only phases present were Zr and the monoiodide.³

In the present work the activities of Zr , ZrI_4 , ZrI_2 , and I over solid zirconium iodides were calculated as functions of solid composition by a Gibbs-Duhem treatment of the measured pressures of ZrI_4 . The activities were then used to derive enthalpies of formation for stoichiometric solid ZrI , ZrI_2 , and ZrI_3 . Equilibrium data were not available for the composition range $\text{ZrI}_{3.43}$ - $\text{ZrI}_{4-\gamma}$, and the solid solution regions. The assumptions and approximations required for calculations in the absence of experimental information have been taken into account in the uncertainties of derived activities and enthalpies of formation.

CALCULATIONAL PROCEDURES AND RESULTS

Activities of Zr and ZrI_4

Zirconium (component 1) and ZrI_4 (component 2) were taken to be the components of the Zr-I system. The pure solid at the temperature in

question was used as the standard state for each component. The activity of ZrI_4 in a two-solid-phase region at a given temperature was calculated as $a_2 = p_2/p_2^\circ$, where p_2 was derived from the data of Table II, and p_2° was the pressure of ZrI_4 over pure, congruently vaporizing $\text{ZrI}_4(\text{s})$, calculated from the relationship of Cubicciotti et al.¹

$$\log p_2^\circ(\text{atm}) = -\frac{1}{4.575} [31880T^{-1} - 49.7 + 6.68 \times 10^{-3}T - 1.131 \times 10^{-6}T^2 + 8.06 \times 10^{-4}T^{-2}] \quad [2]$$

(450-670 K)

The activity of Zr was derived by a Gibbs-Duhem integration. To facilitate this integration, the function α_2 was used:⁶

$$\alpha_2 = \frac{\ln \gamma_2}{(1 - x_2)^2} = \frac{\ln(a_2/x_2)}{(1 - x_2)^2} \quad [3]$$

where γ_2 is the activity coefficient defined as $\gamma_2 = \frac{a_2}{x_2}$ and x_2 is the mole fraction of ZrI_4 in the system. For a system of composition $\text{ZrI}_n, x_2 = \frac{n}{4}$. In terms of α_2 , the activity coefficient γ_1 of Zr at composition x_1' is⁶

$$\ln \gamma_1 = -\alpha_2 x_1' (1 - x_1') - \int_1^{x_1'} \alpha_2 dx_1 \quad [4]$$

In a two-solid-phase region for which isothermal ZrI_4 pressure data are available,

$$\begin{aligned} \int_{x_1'}^{x_1''} \alpha_2 dx_1 &= \int_{x_1'}^{x_1''} \left[\frac{\ln(a_2/x_2)}{x_1^2} \right] dx_1 \\ &= \left[\left(\frac{-1}{x_1} \right) \ln a_2 + \ln(x_1) + \frac{(1 - x_1)}{x_1} \ln(1 - x_1) \right]_{x_1'}^{x_1''} \end{aligned} \quad [5]$$

where x_1' and x_1'' are the composition limits of the two-solid-phase region.

The few pressure values reported in the literature for one-solid-phase region^{2,3} of the Zr-I system were considered unreliable because of the probable lack of equilibrium in effusion cells containing a

a solid phase whose composition changed as ZrI_4 was removed. In these regions the function α_2 was approximated by the polynomial expression

$$\alpha_2 = \frac{\ln \gamma_2}{x_1} = b + c x_1 \quad [6]$$

Analytical expressions of this form have been found to describe the properties of many solid phases over considerable ranges of composition.⁷ The parameters b and c for a given phase, evaluated from the values of α_2 calculated at the phase boundaries, are used in the evaluation of the integral of Equation [4] across the phase,

$$\int_{x_1'}^{x_1''} \alpha_2 dx_1 = \left[bx_1 + \frac{c}{2} x_1^2 \right]_{x_1'}^{x_1''} \quad [7]$$

In the case of the Zr-ZrI_6 solid solution phase, the value of α_2 at the composition of ZrI_6 was assumed to apply throughout the phase. Because of the very small composition range of this phase, this assumption led to a small, negligible uncertainty in the activities.

The activities of Zr and ZrI_4 calculated at 700 K from the data of Tables I and II are shown in Table III. At this temperature, $p_2^\circ = 0.937$ atm.¹ The composition of ZrI_6 assumed for calculation purposes was not critical, and the value $\delta = 4 \times 10^{-3}$ was chosen. The two sets of activity values for the composition $\text{ZrI}_{3.0}$ were derived using the limiting cases for the experimentally unavailable activity of ZrI_4 in the $\text{ZrI}_{3.43} - \text{ZrI}_{4-\gamma}$ two-solid-phase region. The smallest possible value for ZrI_4 activity in this region is its value in the $\text{ZrI}_{2.1} - \text{ZrI}_{2.83}$ region, and the greatest value is that of pure $\text{ZrI}_4(\text{s})$.

Heat Capacities, Entropies, and Tempered Gibbs Energy Functions for the Zirconium-Iodine System

Values of the heat capacities, C_p ; entropies, S° ; and tempered Gibbs energy functions (often called the free energy functions), $\Phi_{298} = -\frac{(G^\circ - H_{298}^\circ)}{T}$ of $\text{Zr}(\text{s})$ and $\text{I}_2(\text{g})$ were taken from the JANAF Tables.⁸ For $\text{ZrI}_4(\text{s})$, the heat capacity and entropy values of Cubicciotti, Lau, and Ferrante¹ were used to derive the tempered Gibbs energy function.

No experimental values of these thermodynamic quantities were found for solid ZrI , ZrI_2 or ZrI_3 . They were estimated by the method used by the authors of the JANAF Tables⁸ for ZrCl_2 and ZrCl_3 as follows. For the solid compound ZrI_n where $n = 1, 2$, or 3 , the quantity Q ($Q = C_p^\circ$, S_T° , or $\Phi_{2,98}^\circ$) was estimated by subtracting $(4-n)$ iodine gram-atomic contributions from the molal quantity for $\text{ZrI}_4(\text{s})$ according to the relationship

$$Q(\text{ZrI}_n, \text{s}) = Q(\text{ZrI}_4, \text{s}) - \left(\frac{4-n}{4}\right)[Q(\text{ZrI}_4, \text{s}) - Q(\text{Zr}, \text{s})] \quad [8]$$

We estimate the uncertainties introduced by this procedure are ± 1 cal/mole degree for C_p and ± 2 cal/mole degree for both S° and $\Phi_{2,98}^\circ$. Table IV presents the thermodynamic properties of the solid zirconium iodides as functions of temperature.

Activity of $\text{I}_2(\text{g})$ and $\text{I}(\text{g})$

In many applications zirconium is exposed to attack by gaseous iodine, and values of the activity of $\text{I}(\text{g})$ and $\text{I}_2(\text{g})$ over zirconium iodide solids are needed to understand the resulting chemical behavior. When ZrI_4 and Zr activities were known, the activity of $\text{I}_2(\text{g})$ with reference to the 1-atm perfect-gas standard state was calculated from the equilibrium

for which

$$\Delta G^\circ = RT \ln K = RT \ln \frac{a_{\text{Zr}} a_{\text{I}_2}^2}{a_{\text{ZrI}_4}} \quad [10]$$

and

$$a_{\text{I}_2} = \left(\frac{K a_{\text{ZrI}_4}}{a_{\text{Zr}}} \right)^{1/2} \quad [11]$$

The standard Gibbs energy change for [9] was calculated using tabulated values of $\Phi_{2,98}^\circ$ and $\Delta H_{2,98}^\circ$.^{1,8} At 700 K,

$$K = 1.02 \times 10^{-30}$$

The activity of monatomic iodine was calculated from the equilibrium constant K_I for the reaction

$$K_I = a_I^2 / a_{I_2} \quad [13]$$

at 700 K, $K_I = 1.13 \times 10^{-6}$.

Activities of Species in Equilibrium with $ZrI_4(s)$

The activities of gaseous species in equilibrium with stoichiometric solid ZrI_4 were calculated at 700 K as follows. Thermodynamic data was used to calculate ΔG° for reaction [12] and for

Equilibrium constants were derived from the relationship $\Delta G^\circ = -RT \ln K$. For pure solid ZrI_4 the activity of $ZrI_4(s)$ was unity, and the only significant source of iodine species was assumed to be from the decomposition of ZrI_4 to $ZrI_3(g)$, for which, since $a_{ZrI_4} = 1$,

$$K = a_{ZrI_3} a_{I_2}^{1/2} \quad [15]$$

For such a decomposition in a closed system, the conservation of mass entails the equality $p_{ZrI_3} = 2p_{I_2} + p_I$. Under the conditions involved, the activities of gaseous I_2 , I , and ZrI_3 with reference to the gas standard state are equal to the respective partial pressures; hence the mass balance becomes,

$$a_{ZrI_3(g)} = 2 a_{I_2} + (K_I a_{I_2})^{1/2} \quad [16]$$

where K_I is the equilibrium constant for Equation [12]. Substitution of Equation [16] into Equation [15] yielded a value of 1.13×10^{-12} for the activity of I_2 at 700 K. For this value of a_{I_2} , the activity of $ZrI_3(g)$ was 1.13×10^{-9} , and the activities of the species ZrI_2 , ZrI , and Zr were all less than 10^{-21} , therefore, the assumption that led to Equation [16] was valid.

Since the activities of ZrI_4 and I_2 were known for the solid composition ZrI_4 , the other activities at this composition shown in Table III could be calculated. The zirconium activity, calculated from the equilibrium constant for the equation

was of particular interest since it placed a lower limit on a_{Zr} over solid ZrI_4 derived by the Gibbs-Duhem integration procedure outlined above. In particular, the activity of Zr in the two-solid-phase region $\text{ZrI}_{3.43}\text{-ZrI}_4\text{-}\gamma$ was calculated to be greater than or equal to that over pure $\text{ZrI}_4(\text{s})$ only when ZrI_4 activities in the two two-solid-phase regions $\text{ZrI}_{2.1}\text{-ZrI}_{2.83}$, and $\text{ZrI}_{3.43}\text{-ZrI}_4\text{-}\gamma$ fell within certain related limits. If the ZrI_4 activity in the region $\text{ZrI}_{3.43}\text{-ZrI}_4\text{-}\gamma$ was equal to that over pure ZrI_4 , then a_{ZrI_4} must be about 0.34 in the range $\text{ZrI}_{2.1}\text{-ZrI}_{2.83}$. This implied a ZrI_4 pressure considerably larger than the measurements of Bhatti et al.⁵ Conversely, if the data of Bhatti are accepted, then the activity of ZrI_4 in the region $\text{ZrI}_{3.43}\text{-ZrI}_4\text{-}\gamma$ must be 4×10^{-2} . Because of the nature of the present calculations, particularly as related to Equation [6], we have not attempted to estimate the activities in the composition range between $\text{ZrI}_{2.83}$ and $\text{ZrI}_{3.43}$. Values for the activities of $\text{ZrI}_{2.83}$ and ZrI_4 were used to calculate $\Delta H_{298}^\circ(\text{ZrI}_3, \text{s})$. The relatively large uncertainty in $\Delta H_{298}^\circ(\text{ZrI}_3, \text{s})$ resulted from this procedure.

Enthalpies of Formation of Solid ZrI , ZrI_2 , and ZrI_3

The Gibbs energy change, ΔG° , for formation of solid ZrI_n ($n = 1, 2, 3$, or 4) from solid Zr and ZrI_4 by the reaction

was obtained from the activities of Zr and ZrI_4 at the composition ZrI_n (where $x_2 = \frac{n}{4}$); we used the relationship

$$\Delta G^\circ = -RT \ln \left[a_{\text{ZrI}_4} / \left(a_{\text{Zr}} \right)^{\frac{4-n}{4}} \left(a_{\text{ZrI}_4} \right)^{\frac{n}{4}} \right] \quad [19]$$

or, since the ZrI_n activity of pure $\text{ZrI}_n(\text{s})$ is unity,

$$\Delta H^\circ = RT \ln \left(a_{\text{Zr}} \right)^{\frac{4-n}{4}} \left(a_{\text{ZrI}_4} \right)^{n/4} \quad [20]$$

The value ΔG° was used to find ΔH_{298}° for ZrI_n by the equation

$$\begin{aligned} \Delta H_{298}^\circ(\text{ZrI}_n, \text{s}) = \Delta G^\circ + T \left[\Phi_{298}^\circ(\text{ZrI}_n, \text{s}) - \frac{n}{4} \Phi_{298}^\circ(\text{ZrI}_4, \text{s}) \right. \\ \left. - \frac{4-n}{4} \Phi_{298}^\circ(\text{Zr}, \text{s}) \right] + \frac{n}{4} \Delta H_{298}^\circ(\text{ZrI}_4, \text{s}) \end{aligned}$$

Activities of ZrI_4 and Zr at 700 K were used to evaluate the enthalpies of formation. For ZrI , the activities used were those for the composition $\text{ZrI}_{1.05} \pm 0.1$. This procedure was justified by the uncertainty in the I/Zr ratio. For ZrI_2 , activities were derived from Equations [4], [5], and [6]. As discussed above, data for $\text{ZrI}_{2.83}$ and ZrI_4 were used to set limits for the activities at ZrI_3 .

The values found for $\Delta H_{298}^\circ(\text{ZrI}, \text{s}) = -34.0 \pm 2.5$ kcal/mole, $\Delta H_{298}^\circ(\text{ZrI}_2, \text{s}) = -66.4 \pm 2.5$ kcal/mole; and $\Delta H_{298}^\circ(\text{ZrI}_3, \text{s}) = -93.6 \pm 4.5$ kcal/mole. For purposes of comparison, for $\text{ZrI}_4(\text{s})$, $\Delta H_{298}^\circ = -116.8 \pm 1.5$ kcal/mole.¹ The uncertainties in ΔH_{298}° for $\text{ZrI}(\text{s})$ and $\text{ZrI}_2(\text{s})$ are essentially due to uncertainties in Φ_{298}° ; the greater uncertainty in activities increased the uncertainty in $\Delta H_{298}^\circ(\text{ZrI}_3, \text{s})$.

REFERENCES

1. D. D. Cubicciotti, K. H. Lau, and M. J. Ferrante, J. Electrochem. Soc., 125, 972 (1978).
2. D. D. Cubicciotti and K. H. Lau, J. Electrochem. Soc., 126, 771 (1979).
3. D. D. Cubicciotti and K. H. Lau, to be published.
4. R. L. Daake and J. D. Corbett, Inorg. Chem., 17, 1197 (1978).
5. M. A. Bhatti, D. B. Copley, and R.A.J. Shelton, J. Less-Common Metals, 55, 293 (1977).
6. L. S. Darken and R. W. Gurry, Physical Chemistry of Metals, p. 264, McGraw-Hill Book Co., New York (1953).
7. L. Brewer, Report LBL-5485, Lawrence Berkeley Laboratory, Berkeley, California (1978), p. 59.
8. JANAF Thermochemical Tables, NSRDS-NBS 37, U.S. Govt. Printing Office, Washington, D.C. (1971), and supplements.

Table I

COMPOSITION LIMITS OF SOLID PHASES OF THE
ZIRCONIUM-IODINE SYSTEM

Nominal Phase	Composition Range		Reference
Zr	Zr	-ZrI ₈	-
ZrI	ZrI _{1.05} ± .10	-ZrI _{1.30} ± .10	2
ZrI ₂	ZrI _{1.9} ± .10	-ZrI _{2.1} ± .10	2
ZrI ₃	ZrI _{2.83} ± .05	-ZrI _{3.43} ± .05	4
ZrI ₄	ZrI ₄ -γ	-ZrI _{4+ε}	-

Table II

PRESSURES OF ZrI_4 OVER TWO-SOLID-PHASE REGIONS OF THE
ZIRCONIUM-IODINE SYSTEM

$$\text{Log}_{10}P(\text{atm}) = -AT^{-1} + B$$

Two-Solid- Phase Region	A	B	T Range, K	Reference
$\text{Zr} - \text{ZrI}_{1.05}$	13217	12.83	735-780	3
$\text{ZrI}_{1.3} - \text{ZrI}_{1.3}$	9308	8.84	660-720	2
$\text{ZrI}_{2.1} - \text{ZrI}_{2.83}$	8700	10.45	586-641	5 [†]

[†]Reference 5 assigned the data to the composition range $\text{ZrI}_{3.0} - \text{ZrI}_{3.2}$. The present assignment is from Reference 2.

Table III

ACTIVITIES OF ZrI_4 , Zr , I_2 , AND I IN EQUILIBRIUM WITH
 CONDENSED PHASES OF COMPOSITION ZrI_n AT 700 K
 Standard States: Zr(s) , $\text{ZrI}_4(\text{s})$, $\text{I}_2(\text{g})$, I(g)

n	a_{ZrI_4}	a_{Zr}	a_{I_2}	a_{I}
$\gamma - 1.05 \pm 0.1$	9.7×10^{-5}	1.00	9.8×10^{-19}	1.0×10^{-12}
$1.30 \pm 0.1 - 1.9 \pm 0.1$	3.7×10^{-5}	0.22	1.3×10^{-17}	3.8×10^{-23}
2.00	8.5×10^{-4}	1.1×10^{-2}	2.8×10^{-16}	1.8×10^{-11}
$2.1 \pm 0.1 - 2.83 \pm 0.5$	1.2×10^{-2}	6.9×10^{-4}	4.2×10^{-15}	6.9×10^{-11}
3.00	1.2×10^{-2}	6.9×10^{-4}	4.2×10^{-15}	1.1×10^{-11}
	1	8.0×10^{-7}	1.1×10^{-12}	1.1×10^{-9}
4.00	1	8.0×10^{-7}	1.1×10^{-12}	1.1×10^{-9}

Table IV

HEAT CAPACITIES, ENTROPIES, AND TEMPERED GIBBS ENERGY FUNCTIONS
(cal/degree·mole) FOR SOLID ZrI ,[†] ZrI_2 ,[†] ZrI_3 ,[†] and ZrI_4 ^{*}

ZrI(s)			
T, K	C_p°	S_T°	$\bar{G}_{298}^\circ$
298	12.03	21.94	21.94
300	12.05	22.02	21.94
400	12.43	25.54	22.42
500	12.77	28.35	23.34
600	13.09	30.71	24.38
700	13.39	32.75	25.43
800	13.71	34.55	26.45

$\text{ZrI}_2(\text{s})$			
T, K	C_p°	S_T°	$\bar{G}_{298}^\circ$
298	17.98	34.56	34.56
300	18.01	34.68	34.56
400	18.50	39.93	35.28
500	18.90	44.10	36.63
600	19.26	47.58	38.18
700	19.61	50.58	39.74
800	19.95	53.21	41.26

$\text{ZrI}_3(\text{s})$			
T, K	C_p°	S_T°	$\bar{G}_{298}^\circ$
298	23.94	47.18	47.18
300	23.96	47.34	47.18
400	24.56	54.31	48.13
500	25.03	59.84	49.94
600	25.44	64.44	51.98
700	25.85	68.39	54.05
800	26.17	71.87	56.06

$\text{ZrI}_4(\text{s})$			
T, K	C_p°	S_T°	$\bar{G}_{298}^\circ$
298	29.90	59.80	59.80
300	29.92	59.99	59.81
400	30.63	68.70	60.98
600	31.16	75.59	63.24
600	31.61	81.32	65.79
700	32.04	86.22	68.37
800	32.44	90.52	70.87

[†]Estimated (see text).

^{*}Reference 1.

Appendix H

CHEMISORPTION OF IODINE ON ZIRCONIUM

By

Gopala N. Krishnan, Bernard J. Wood, and Daniel Cubicciotti

SRI International
Menlo Park, California 94025

ABSTRACT

Auger electron spectroscopy was used to observe the relative coverage of iodine on the surface of a zirconium crystal exposed to a flux of iodine gas molecules. The zirconium was heated to temperatures of 1000 to 1300 K, and the iodine pressures corresponded to 10^{-4} to 10^{-6} Pa (10^{-9} to 10^{-11} atm). Iodine was found to chemisorb on the surface, the isotherms corresponded to the Temkin model. Isotherms derived from these isotherms showed a logarithmic dependence of pressure on reciprocal temperature. The slopes of the isotherms indicated an enthalpy of formation of the surface layer of about 60 kcal/mole. The thermodynamics of formation of an iodine adspecies on a zirconium surface were compared with the thermodynamics of formation of zirconium monoiodide, the lowest solid iodide of zirconium.

INTRODUCTION

The iodine-induced stress corrosion cracking (SCC) of zirconium involves chemical reactions between clean zirconium surface and iodine-containing species.¹ That is, in the SCC process, fresh metal surface is created as cracks grow. The freshly formed surface apparently reacts with iodine-containing species in the system as evidenced by the fact that the topography of the cracks formed in the metal and the stresses required to form and extend the cracks are different in an iodine-containing environment than in a noniodine containing environment. Consequently adsorption of iodine-containing species at the crack tip is likely to be the critical chemical reaction in the SCC process. Such a surface reaction would weaken the Zr-Zr bonds in certain crystallographic planes in the metal, leading to the observed effects of iodine on the failure process.

The reaction of iodine-containing species with clean zirconium surfaces is therefore central to the mechanism of iodine-induced SCC of zirconium alloys; however, no studies have been made of this reaction. The rates of reaction of iodine with zirconium have been studied but under conditions in which the metal was covered by surface layers of zirconium iodides.¹⁻³

In the present study, Auger electron spectroscopy (AES) was used to monitor the surface of a clean zirconium foil exposed to a flux of iodine vapor. The AES technique provided a quantitative measurement of the concentration of iodine chemisorbed on the surface as a function of zirconium temperature and iodine flux. The results showed that iodine was chemisorbed by the zirconium surface even at high temperatures.

EXPERIMENTAL PROGRAM

AES is a surface-sensitive analytical technique that has been used extensively to study gas-metal interactions at the monolayer levels.⁴ During AES analysis, the specimen is bombarded with a medium energy (~ 3 keV) electron beam, which causes secondary electron emission from

the specimen. Some of these secondary electrons consist of Auger electrons arising from electronic transitions in the atoms present in the specimen. The technique is surface sensitive because of the limited escape depth of the Auger electrons. For electron energies from 50 to 500 eV, the range of interest in this study, the analysis depth varies from 0.5 to 1 nm.

The concentration of a particular elemental component in the near-surface atomic layer of a specimen determines the amplitudes of the peaks in its Auger spectrum. But the proportionality factor relating concentration to peak amplitude, frequently referred to as the Auger yield, is a complex quantity that cannot be precisely evaluated from first principles.⁴ However, changes in concentration of a component can be followed with good precision by measuring the growth or decay of an Auger peak.

Apparatus and Materials

All experiments were conducted in an ultrahigh vacuum system capable of attaining 10^{-8} Pa base pressure. The AES analyses were performed with a Varian cylindrical mirror analyzer with an integral electron gun. The incident electron beam was ~ 100 μm in diameter at the specimen and was normally operated at 3000 eV and 5 μA . The total pressure in the system was measured with an ionization gauge, and the partial pressures of gas components were determined with a quadrupole mass spectrometer. A rastered, 3-keV argon ion beam was used to clean the specimen surface. The arrangement of the various components with respect to the specimen is shown in Figure 1.

The specimen used in this study was a high purity zirconium foil 0.0127 cm thick and ~ 0.3 cm wide. The strip was resistively heated, and its temperature was monitored by a chromel-alumel thermocouple spot-welded to the back of the specimen at its midpoint. A 0.01-cm-diameter area in the center of the specimen was analyzed by the Auger electron spectrometer.

SA-5780-29

FIGURE 1 SCHEMATIC DIAGRAM OF APPARATUS

Iodine was introduced into the vacuum chamber through a glass-lined stainless steel capillary tube* (~ 0.4 mm ID x 90 cm long). The upstream end of the capillary tube was attached to a Pyrex glass manifold by means of a Cajon ultra-torr stainless steel vacuum connector. This small connector was the only metal surface in contact with the iodine vapor. The iodine reservoir could be isolated from the capillary by means of a Viton sealed glass valve. The iodine manifold, was heated when necessary by a heating tape and could be evacuated through a liquid nitrogen-cooled, molecular sieve trap into a mechanical pump. Before the experiment began, the iodine reservoir was filled with resublimed iodine by vacuum distillation through a molecular sieve trap to remove traces of water. The reservoir, equipped with a break-seal tubulation, was pulled-off from the distillation manifold and subsequently attached to the capillary inlet manifold. Immediately before the experiment began, the break seal was fractured to admit iodine into the manifold.

The outlet end of the capillary tube was pointed at the specimen and situated about 0.2 cm from its surface. On the basis of our measurements with oxygen with a similar arrangement,⁵ we estimate that 70% of the gas molecules leaving the capillary tube strike the specimen.

Procedure

The mass flow rate of iodine through the capillary tube was determined by the pressure of iodine in the manifold and by the conductance of the capillary tube. The pressure of iodine in the manifold was controlled by immersing the reservoir in various freezing bath mixtures designed to maintain constant subambient temperatures. The baths used and the attained temperatures are listed in Table 1. The iodine manifold and the capillary tube were initially degassed at 400 K overnight. The

*Supplied by Scientific Glass Engineering, Inc.,
Austin, Texas 78759.

Table 1

TEMPERATURE OF IODINE BATH AND EQUIVALENT IODINE
PRESSURE NEAR THE SPECIMEN

Bath	Bath Temperature (K)	Iodine Vapor Pressure (Pa)	Mass Flow Rate Through Capillary $\text{Pa} \cdot \text{L} \cdot \text{sec}^{-1}$	Iodine Pressure at the Specimen ^a (Pa)
CCl_4 solid-liquid	252.7	4.34	3.04×10^{-5}	5.9×10^{-6}
Saturated KCl-ice	263.7	11.9	8.31×10^{-5}	1.6×10^{-5}
Ice-water	273.2	26.9	1.83×10^{-4}	3.6×10^{-5}
p-dioxane solid- liquid	281.2	48.4	3.39×10^{-4}	6.6×10^{-5}

^aPressure equivalent of collision rate averaged over area of specimen that intercepts 70% of iodine molecules leaving the capillary.

iodine reservoir was kept at the bath temperature for two hours before the iodine valve was opened to admit iodine to the manifold and to the vacuum chamber.

The zirconium specimen surface was cleaned by a combination of argon ion sputtering and high temperature treatment. After initial sputtering, we found that holding the specimen at 1200 K was sufficient to maintain a relatively clean surface. During the start of the experiment, the specimen was cooled from 1200 K to the selected reaction temperature, and the capillary inlet valve was opened to admit iodine to the specimen surface. After a steady-state coverage was attained, the temperature of the specimen was increased to a higher temperature while a constant iodine reservoir temperature was maintained.

The iodine pressure near the specimen can be computed from the mass flow rate, $\dot{m}$, of iodine passing through the capillary tube by the following equation derived from kinetic theory of gases:

$$\bar{P} = \frac{4k\dot{m}RT}{a\bar{c}} \quad (1)$$

where a = area of the specimen

$\dot{m}$ = mass flow rate

$\bar{P}$ = equivalent pressure

$\bar{c}$ = mean molecular velocity

T = gas temperature.

k = fraction of molecules leaving the capillary that strike the specimen surfaces.

The mass flow rate of iodine through the capillary tube is proportional to its conductance and to the pressure at the inlet end

$$\dot{m} = P \cdot c \quad (2)$$

where P = manifold pressure and c = capillary conductance.

The iodine pressure in the manifold is equal to the vapor pressure of iodine at the reservoir bath temperature. The conductance of the capillary was determined in a separate experiment in which the manifold

was connected to a Validyne stainless steel diaphragm pressure gauge. Iodine was introduced from the reservoir into the manifold of calibrated volume, V , up to a chosen pressure, P , and then the reservoir valve was shut off. From the observed rate of pressure decrease, dP/dt , due to iodine flowing through the capillary tube, the conductance, c , of the capillary was calculated from the following relation:

$$c = \frac{V}{P} \frac{dP}{dt} \quad (3)$$

the conductance of the capillary tube was found to have a constant value of 6.4×10^{-6} liters s^{-1} over an iodine pressure range of 13.3 to 66.7 Pa.

RESULTS AND DISCUSSION

Auger electron spectra in the range of 70 to 570 eV were recorded at suitable intervals at various specimen temperatures and iodine pressures. Table 2 summarizes the Auger peaks and transitions of interest.⁶ Figure 2 shows representative Auger spectra at different specimen temperatures. The major peaks of iodine at 504 eV and 515 eV closely bracket the major oxygen peak at 510 eV. Hence, if oxygen is a significant component on the specimen surface, overlap would occur between the oxygen peak and these iodine peaks. To eliminate oxygen interference, we used high specimen temperatures at which oxygen accumulation on the surface was minimal,⁵ as confirmed by the absence of the AES oxygen peak under these conditions. Examining the ratios of the iodine peak heights provided further evidence. (Peak heights are represented by the symbol: $A_{\text{element, energy}}$.) We found that values of the ratios $A_{\text{I } 504}/A_{\text{I } 515}$ did not change significantly with variations in the iodine pressure and the specimen temperature. Thus, any contribution of oxygen to the iodine 504-eV peak was negligible under our experimental conditions.

The zirconium and iodine Auger peaks do not appear to shift in energy with iodine coverage on the surface (Figure 2). The absence of any energy shifts suggests that the iodine observed on the zirconium surface, at the high temperatures and the low iodine pressures used, is

Table 2

AUGER ELECTRON ENERGIES^a

<u>Element</u>	<u>Transition</u>	<u>Kinetic Energy (eV)</u>
Zr	M ₅ N ₂ N _{2,3}	92
	M ₅ N _{2,3} N _{2,3}	117
	M ₄ N ₂ V	127
	M ₄ N _{2,3} N _{4,5}	147
	M ₅ N _{4,5} N _{4,5}	175
I	M ₅ N ₁ N _{4,5}	369
	M ₄ N ₁ N _{4,5}	389
	M ₄ N ₂ N _{4,5}	434
	M ₅ N _{4,5} N _{4,5}	507
	M ₄ N _{4,5} N _{4,5}	515
	M ₅ N ₅ N ₇	560
	M ₄ N ₅ N ₇	570
O	KL ₁ L ₁	475
	KL ₁ L ₂	490
	KL ₂ L ₂	510
C	KL ₂ L ₂	274

^aReference 6

SA-5780-30

FIGURE 2 TYPICAL AUGER ELECTRON SPECTRA OF ZIRCONIUM FOIL EXPOSED TO IODINE VAPOR AT VARIOUS TEMPERATURES

is present in a chemisorbed state, in contrast to being combined in a surface or bulk compound.

Figure 3 illustrates the change in the ratio $A_{I\ 504}/A_{Zr\ 92}$ as a function of iodine pressure at different specimen temperatures. This ratio of iodine to zirconium peak heights is a relative measure of the coverage of iodine on the surface. Normalization of the iodine peak to this stable core-level zirconium peak compensates for random variations in instrumental parameters such as incident electron beam current, electron multiplier gain, and the position of the specimen with respect to the focal point of the electron energy analyzer. As the temperature was decreased, the normalized iodine signal appeared to approach an asymptote with a value of $A_{I\ 504}/A_{Zr\ 49} \approx 1.2$, suggesting an upper limit in coverage. Under the high temperatures and low iodine pressures used in these experiments, such a coverage limit is likely to be less than a monolayer of the adspecies.

We attempted to establish unequivocally an iodine signal intensity that corresponded to monolayer coverage by taking the Zr crystal to much lower temperatures while exposing it to a high iodine flux. Our effort was thwarted by the appearance of a significant oxygen signal at temperatures below 960 K. Carbon also appeared on the surface and increased significantly at lower temperatures. We concluded that these impurities originated in the bulk of the specimen because the background pressure in the vacuum chamber was too low ($\sim 10^{-8}$ Pa) to populate the surface to the observed impurity levels within the duration of the experiments. Although the general appearance of the curves in Figure 3 is similar to the Langmuir isotherm, a critical plot of the data showed they deviated significantly from the Langmuir equation. That is, a plot of $A_{I\ 504}/A_{Zr\ 92}$ divided by pressure of iodine versus pressure of iodine was not linear as it would be for the Langmuir form of isotherm.⁷ The results in the temperature range 1023 to 1323 K, however, were equally well fit by the Freundlich equation⁷ [proportionality of $\log (A_{I\ 504}/A_{Zr\ 92})$ versus $\log P(I_2)$] and by the Temkin equation [proportionality of $(A_{I\ 504}/A_{Zr\ 92})$ versus $\log P(I_2)$]. Figure 4 shows the results of the Temkin plot.

SA-5780-31

FIGURE 3 ADSORPTION ISOTHERMS FOR IODINE ON ZIRCONIUM

The smoothed isotherms of Figure 4 were used to obtain the pressures of iodine in equilibrium with three different surface coverages, corresponding to $(A_I 504/A_{Zr 92})$ of 0.2, 0.4, and 0.8. Graphs of the log of iodine pressure versus reciprocal of absolute temperature for these isosteres are shown in Figure 5 to be good straight lines.

On the basis of the experimental results, we postulate that the interaction between gaseous molecular iodine and metallic zirconium involves the following mechanistic model. At the gas pressures (10^{-4} Pa or less) and surface temperatures (1000 to 1300 K) used, molecular iodine is thermodynamically unstable with respect to monatomic iodine. Hence, the iodine molecules that strike the metal surface and become thermalized will dissociate; therefore the iodine can be assumed to be monatomic in its interaction with the zirconium. The iodine striking the surface either adheres to form an adsorbed layer on the metal or is evaporated into the gas. The iodine that adheres to the surface forms a chemisorbed layer from which volatile species can then evaporate. Such a model is consistent with the results of studies of the evaporation of halides from metal surfaces exposed to halogen gases. It has been shown that the processes can be represented by the following steps: (1) the incident molecules adsorb dissociatively, (2) surface reactions occur between the adsorbed species and surface metal, and (3) the reaction products evaporate. The atom ratios of the species that evaporate were found to be in good accord with values calculated from equilibrium thermodynamics for several transition metal-halide systems.⁸⁻¹¹

To apply this model to the present system requires an evaluation of the equilibrium partial pressures of the gaseous species. The thermodynamic information required¹²⁻¹⁵ to evaluate the partial pressures in equilibrium with zirconium metal are available.⁸ The calculation shows that the predominant species is exclusively monatomic iodine. At the lowest temperature (1000 K) and highest pressure (10^{-4} Pa) considered, there was a small contribution by ZrI_4 gas, which amounted to about 0.1% of the iodine atom pressure. The pressures of all other species were smaller.

SA-5780-32

FIGURE 4 ADSORPTION ISOTHERMS, TEMKIN PLOT

SA-5780-33

FIGURE 5 ADSORPTION ISOSTERES, I_2/Zr

Points taken from curves of Figure 3 at three values of $A_{I\ 504}/A_{Zr\ 92}$: ○: 0.2; △: 0.4; □: 0.8.

The interaction model and the equilibrium gas pressures calculation show that it is now reasonable to treat the system in terms of the equilibrium between a monatomic iodine gas and a chemisorbed layer of iodine on the zirconium surface. Thus, the data presented in Figure 5 relate to the equation

in which θ represents a fixed surface coverage and is proportional to $A_{\text{I } 504}/A_{\text{Zr } 92}$, referred to below as θ' .

The solid zirconium iodide in equilibrium with zirconium metal has the composition $\text{ZrI}_{1.05}$, which can be considered to be the monoiodide (ZrI).¹⁶ Its enthalpy of formation has been evaluated, and its absolute entropy has been estimated so that for the equilibrium

we can specify the standard free energy change ΔG° :

$$\Delta G^\circ = -59,500 + 30.5 T \text{ (kcal/mole)}. \quad (6)$$

We can then calculate the equilibrium partial pressure of monatomic iodine:

$$\log P(\text{I, atm}) = -13,000/T + 6.67. \quad (7)$$

Interestingly, the coefficient of the reciprocal temperature term (proportional to the enthalpy change for the reaction) corresponds to the slope of the lines drawn through the data points in Figure 5. Thus the enthalpy change for reaction (4) is the same as that for reaction (5) and we can write the following equations from the data in Figure 5:

$$\log P(\text{I, atm}) = -13,000/T + 2.44 \text{ (for } \theta' = 0.8) \quad (8)$$

$$\log P(\text{I, atm}) = -13,000/T + 1.20 \text{ (for } \theta' = 0.4) \quad (9)$$

$$\log P(\text{I, atm}) = -13,000/T + 0.51 \text{ (for } \theta' = 0.2) \quad (10)$$

Thus, for the three levels of iodine coverage, the enthalpy change for chemisorption, considered in terms of formation of surface ZrI, is the same as the enthalpy of formation of solid ZrI. The differences in the thermodynamics of formation of the solid and the chemisorbed state lie in the entropies of the reactions and indicate that the chemisorbed ZrI species have substantially larger absolute entropies than the crystalline solid.

In relation to the problem of SCC of zirconium alloys, the present results show that iodine chemisorbs on clean zirconium surfaces. Thus fresh zirconium surfaces would chemisorb iodine and would be capable of attracting iodine from solid zirconium iodides deposited on nearby surfaces. The driving force for transfer of iodine from solid zirconium iodide to a partially covered zirconium surface would be given by the difference between equation (7) and equation (10) for the smallest coverage studied. That driving force can be expressed as a free energy change; namely,

$$\Delta G(\text{iodine transfer}) = (6.67 - 0.51) 4.575 T = .28 T \text{ cal/mole.}$$

CONCLUSIONS

We have shown from Auger electron spectroscopy measurements that a heated zirconium surface exposed to iodine vapor acquires a chemisorbed layer of iodine. The variation with iodine pressure of fractional coverage of the zirconium surface can be fitted to a Temkin model. Interpreted in terms of an equilibrium thermodynamic model, the results suggest that chemisorption of iodine on zirconium at high temperatures involves the formation of a ZrI surface compound.

REFERENCES

1. B. Cox and J. C. Wood, "Corrosion Problems in Energy Conversion and Generation," C. S. Tedmon, Jr., ed. (The Electrochemical Society, Princeton, New Jersey, 1974), p. 275.
2. L. N. Shelest, E. K. Safrnov, and A. S. Mikhailova, Russ. J. Inorg. Chem. 18, 9 (1973).
3. R. M. Horton and R. L. Kinney, "Kinetics of Formation of ZrI_4 from Zr and I_2 ," in Metal-Slag-Gas Reactions and Processes, Z. A. Foroulis and W. W. Smeltzer, eds (Electrochemical Society, Princeton, New Jersey, 1975), p. 217.
4. C. C. Chang, in Characterization of Solid Surfaces, P. F. Kane and G. B. Larrabee, eds. (Plenum Press, New York, 1974), p. 537.
5. G. N. Krishnan, B. J. Wood, and D. Cubicciotti, "Initial Stages in the Oxidation of Zirconium," to be published.
6. Y. E. Strausser and J. J. Uebbing, Chart of Auger Electron Energies (Varian Associates, Palo Alto, 1971).
7. F. C. Tomkins, Chemisorption of Gases on Metals (Academic Press, London, 1978), p. 93.
8. J. L. Philipport, J. Y. Caradec, B. Weber, and A. Cassuto, J. Electrochem. Soc. 125, 162 (1978).
9. B. Weber, J. L. Philipport, and A. Cassuto, Surf. Sci., 52, 311 (1975).
10. J. Y. Carodac, J. L. Philippart, B. Weber, and A. Cassuto, Surf. Sci. 54, 593 (1976).
11. J. C. Batty and R. E. Stickney, J. Chem. Phys., 51, 4475 (1969).
12. P. D. Kleinschmidt, D. Cubicciotti, and D. L. Hildenbrand, J. Electrochem. Soc. 125, 1543 (1978).
13. D. Cubicciotti, K. H. Lau, and M. J. Ferrante, J. Electrochem. Soc. 125, 972 (1978).
14. D. Cubicciotti and K. H. Lau, J. Electrochem. Soc. 126, 771 (1979).
15. D. Cubicciotti and K. H. Lau, "Thermodynamics of Vaporization of ZrI_4 in the Univariant Region Zirconium Monoiodide/Zirconium," J. Electrochem. Soc., to be published.

16. R. H. Lamoreaux and D. Cubicciotti, "Thermodynamic Properties of the Solid Zirconium Iodides," J. Electrochem. Soc., to be published.

Appendix I

INITIAL STAGES OF OXIDATION OF ZIRCONIUM

By

Gopala N. Krishnan, Bernard J. Wood, and Daniel Cubicciotti

SRI International
Menlo Park, California 94025

ABSTRACT

The uptake of oxygen on the surface of an initially clean zirconium crystal was observed by means of Auger electron spectroscopy (AES). This technique permitted measurement of both rate of growth of surface oxygen and the chemical state of the oxygen. Experiments were performed in the temperature range 773 to 1008 K with oxygen pressures from 1.9×10^{-4} to 7.2×10^{-3} Pa. Under these conditions, the rate of diffusion of oxygen into the metal bulk becomes significant, and determines the extent of the chemisorption regime. At the higher temperatures, the chemisorption regime extends to long exposure periods, whereas at the lower temperature, an oxide is rapidly formed. The observed linear rate of oxygen uptake after the appearance of the surface oxide may be caused by oxygen diffusing through an oxide layer of constant thickness and subsequently dissolving in the bulk metal underneath. This oxide layer is estimated to be about 1 nm thick.

INTRODUCTION

In recent studies¹⁻³ of the reaction of zirconium with oxygen at low pressures (10^{-4} to 10^{-1} Pa) and at elevated temperatures ($T > 775$ K), it was demonstrated that the oxygen uptake rate follows a linear rate law for a substantial length of time. After extended periods of exposure, especially at higher pressures, when there has been ample opportunity for the formation of an oxide scale layer, oxygen uptake can be described by a parabolic rate law. Previous investigators have hypothesized that, in the linear rate regime, oxygen uptake is controlled either by arrival rate of oxygen molecules to the surface or by diffusion of oxygen adspecies through a "thin layer" of oxide on the surface.² However, no quantitative information is available on the nature of the rate of formation, or the thickness of such an oxide layer. We have used Auger Electron spectroscopy (AES) to characterize the initial stages of oxidation of zirconium under clean surface, ultrahigh vacuum conditions. For applications where the oxygen gettering quality of zirconium is of interest, the results of this study will permit one to define the conditions of temperature and oxygen pressure that favor bulk dissolution of oxygen in contrast to oxide film (scale) formation.

EXPERIMENTAL PROGRAM

Approach

The use of Auger electron spectroscopy to study initial stages of gas-metal interactions has been well documented.⁴ In this technique, the emission of Auger electrons is stimulated by the bombardment of the specimen with a high-energy (3-kV) electron beam. The emitted Auger electrons are energy analyzed to provide a spectrum of peaks whose positions on the energy scale identify the elemental components on the specimen surface. AES is a highly surface-selective analytical technique because of the limited escape depths of Auger electrons. For electron

energies ranging from 50 to 500 eV., the range of interest in this study, the escape depth of electrons varies between 0.5 to 1 nm,⁵ which is equivalent to two to four atomic layers; hence, components in the bulk metal below this depth will not be detected by AES.

The concentration of a particular elemental component in the near-surface atomic layers of a specimen determines the amplitudes of the peaks in its Auger spectrum. But the proportionality factor relating concentration to peak amplitude, frequently referred to as the Auger yield, is a complex quantity that cannot be precisely evaluated from first principles.⁴ However, changes in concentration of a component can be followed with good precision by measuring the growth or decay of an Auger peak. Thus, we observed the adsorption of oxygen on the zirconium surface by measuring the amplitude of the oxygen Auger peak at 510 eV.

Apparatus and Materials

All experiments were conducted in an ultrahigh vacuum system capable of attaining 10^{-8} Pa base pressure. The AES analyses were performed with a Varian cylindrical mirror analyzer with an integral electron gun. The incident electron beam was ~ 100 μm in diameter at the specimen, and it was normally operated at 3000 eV and 5 μA . The total pressure in the system was measured with an ionization gauge, and the partial pressures of gaseous components were determined with a quadrupole mass spectrometer. A rastered, 3-keV argon gun was used to clean the specimen surface. The arrangement of the various components with respect to the specimen is shown in Figure 1.

Two kinds of specimens were used in this study. Preliminary measurements were made on a 0.0127-cm-thick zirconium foil strip. The strip was heated resistively, and its temperature was monitored by an iron-constantan thermocouple spot-welded to its midpoint.

More extensive measurements were made on a "Marz grade" zirconium crystal, containing ~ 100 ppm oxygen impurity obtained from Materials Research Corporation. This specimen was a disk, spark cut from a 0.63-cm-diameter rod that was nominally a single crystal. However, x-ray

diffraction and metallographic observations revealed that the rod consisted of several large grains. After sequential mechanical and chemical polishing, seven large grains could be delineated on the face of the 1-mm-thick specimen; thus, the average diameter of each grain was about 250 times greater than the AES electron beam diameter. To avoid problems associated with grain-boundary impurities or oxygen transport, we focused the AES beam onto the center of a large grain. The specimen was heated by radiation from a tungsten filament situated beneath it (Figure 1), and the average temperature was measured with an iron-constantan thermocouple spot-welded to the edge of the disk.

Oxygen (Linde UHP grade, 99.99% O_2) was admitted to the vacuum chamber through a calibrated stainless steel capillary tube (75 cm long by 0.017 cm ID). The mass flow rate of gas into the chamber could be precisely controlled and measured, independent of the pressure in the chamber, by adjusting the oxygen pressure at the upstream end of the capillary tube. The downstream (outlet) end of the capillary tube pointed at the specimen surface from a distance of about 0.2 cm. On the basis of mass spectroscopic measurements of mass flux as a function of radial distance from the center line of the capillary tube, we estimated that about 70% of the gas molecules emanating from the tube impinged on the specimen surface.

Procedure

The only detectable impurity on the zirconium crystal surface following cleaning by argon ion bombardment at 1000 K was a trace of oxygen. In the vacuum chamber at 10^{-7} Pa, the surface of the specimen remained clean indefinitely at temperatures above 900 K. At lower temperatures, oxygen accumulated on the surface. The observed rate of accumulation was too fast to be due to adsorption from the gaseous environment in the vacuum chamber ($P_{O_2} \approx 10^{-9}$ Pa); hence, we concluded that dissolved oxygen diffused from the bulk to the surface while the crystal was cooling. Although such a process is highly unlikely, based on the bulk thermodynamics of the Zr- O_2 system, existence of a relatively

SA-5780-19

FIGURE 1 SCHEMATIC DIAGRAM OF APPARATUS

stable oxygen adlayer on a Zr crystal, discussed later, indicates such a surface adlayer might form at the expense of a low bulk concentration of O in Zr. Due to the relatively massive size of the crystal and its poor thermal contact with any heat sink, the specimen could not be quenched from a high temperature to give an oxygen-free surface at temperatures less than 750 K. Consequently, oxygen uptake rate measurements on the zirconium crystal were made only at temperature in the range 750 to 1050 K. In contrast, the zirconium foil strip could be rapidly quenched from 1000 K to room temperature to give a nearly oxygen-free surface on which oxygen was observed to adsorb at a rate proportional to its partial pressure in the vacuum chamber.

After the specimens were cleaned by Argon ion bombardment at 1000 K, the temperature was shifted to the desired level for the experiment by adjusting the power input to the heater. When the specimen temperature became stable (typically within 120 seconds), the capillary inlet valve was opened enough to establish a steady flow of oxygen at a desired level. An equivalent, average, steady-state pressure, P_{O_2} , of oxygen at the specimen surface was calculated from the known mass flow rate, $\dot{m}$, of oxygen through the capillary tube using the following equation derived from the kinetic theory of gases.⁶

$$\alpha \dot{m}/A = P_{O_2} \bar{c}/4RT$$

where $\bar{c}$ is the mean molecular velocity at the gas temperature, T , R is the gas constant, A is the exposed geometric surface area of the specimen, and α is the fraction of molecules that strike the specimen taken to be 0.7 for this geometry. Specimen temperatures and oxygen pressures used in these experiments are summarized in Table 1.

Auger spectra over the energy range 60 to 560 eV were recorded every 30 seconds on an oscillographic chart recorder (Beckman Dynograph, Type RS). Rate data were obtained from this chart by measuring the AES peak height as a function of elapsed time. At longer intervals, the Auger spectrum of the specimen surface was recorded more slowly in order to obtain higher resolution of the Auger peaks.

Table 1
SUMMARY OF EXPERIMENTAL CONDITIONS

Specimen Temperature (K)	O ₂ Flow Rate (molec s ⁻¹ x 10 ⁻¹⁴)	Equivalent O ₂ Pressure, P (Pa x 10 ³)	Maximum Exposure Duration (s)
300	1.8	0.19	500
773	9.3	1.0	900
853	10.2	0.97	1100
933	6.4	0.57	2500
933	64	7.2	2500
963	33	2.7	2000
1008	40	3.6	3000

RESULTS

Auger Spectra

The observed peaks in our experimental study are associated with particular Auger transitions⁷ as shown in Table 2. Figure 2 is a representative sequence of Auger spectra obtained during exposure of a specimen to oxygen at a constant temperature. Besides the obvious increase in the oxygen peak (510 eV) height, there are other features to be noted. The three zirconium peaks that involve valence band electrons (127 eV, 147 eV, and 175 eV) decrease in amplitude with increasing oxygen coverage. At some point during oxygen exposure, a new zirconium Auger peak appears and begins to grow in height. This peak can be interpreted as a 7-eV shift to lower energy of the 147-eV peak. Similar shifts appear for the 175-eV and 127-eV peaks. Such peak shifts are indicative of a change in the chemical state of the zirconium atoms in the specimen surface region. Similar Auger peak shifts during oxide formation have been reported in the case of nickel,⁸ silicon,⁹ molybdenum,¹⁰ iron,¹¹ and aluminum.¹²

In contrast to this behavior, the Auger peaks (92 eV and 117 eV) arising exclusively from core level transitions are less profoundly affected by oxygen uptake. These peaks exhibit a modest shift of about

Table 2

AUGER ELECTRON ENERGIES IN ZR-O₂ SYSTEM

<u>Element</u>	<u>Transition</u> ^a	<u>Kinetic Energy in</u>	
		<u>Metal</u>	<u>Oxide Film</u>
Zr	M ₅ N ₂ N _{2,3}	92	88
	M ₅ N _{2,3} N _{2,3}	117	113
	M ₄ N ₂ V	127	120
	M ₄ N _{2,3} N _{4,5}	147	140
	M ₅ N _{4,5} N _{4,5}	175	167
O ^b	K L ₂ L ₂	-	475
	K L ₁ L ₂	-	490
	K L ₁ L ₂	-	510

^aReference 7^bNo line shift was observed for the oxygen lines.

SA-5780-18

FIGURE 2 CHANGES IN AUGER SPECTRA OF ZIRCONIUM CYRSTAL DURING EXPOSURE TO OXYGEN

$T_{Zr} = 963 \text{ K. } P_{O_2} = 2.5 \times 10^{-3} \text{ Pa.}$

4 eV during oxide formation. This smaller shift attests to the fact that the core level electrons are less affected than the valence level electrons by the chemical environment.

More interestingly, the amplitudes of the core level Auger transition peaks (92 eV and 117 eV) do not change appreciably during oxygen uptake. In fact, within the precision of our experimental measurements, the 92-eV peak showed little change during the entire range of oxygen coverage studied in this investigation. This insensitivity of the zirconium core level peaks to the presence of oxygen was confirmed by obtaining an Auger spectrum of ZrO_2 . In the oxide, the peaks involving valence band electrons are attenuated considerably relative to the peaks involving core levels only. We determined that the ratio of $\text{Zr}(M_5N_2N_{2.3})/\text{Zr}(M_4N_{2.3}N_{4.3})$ is 0.17 in the pure metal and is ~ 1 in the oxide.

Surface Oxygen Growth

We demonstrated that the surface oxygen coverage of the Zr crystal was a linear function of P_{O_2} over a tenfold change in P_{O_2} (see Figure 3). Consequently it is convenient to test oxygen uptake in terms of exposure, which is the product of pressure and time.

The variation in surface oxygen coverage on the zirconium specimens is displayed as a function of oxygen exposure and of temperature in Figure 3. The abscissa of Figure 3 is expanded in Figure 4 to resolve the shape of the curves at small values of exposure. Since the Zr (92 eV) peak height is shown to be insensitive to the presence of oxygen, we have used it as a normalizing factor to compensate for changes in incident electron beam current, electron multiplier gain and the like.

The surface oxygen uptake curves indicate four distinct sequential stages in the accumulation of oxygen on the zirconium surface.

- (1) An initial period of rapid oxygen accumulation.
- (2) A region of slow increase in oxygen level.
- (3) A second period of further rapid oxygen accumulation.
- (4) A constant coverage regime.

FIGURE 3 OXYGEN UPTAKE ON ZIRCONIUM CRYSTAL AS A FUNCTION OF TEMPERATURE AND OXYGEN EXPOSURE

FIGURE 4 OXYGEN UPTAKE ON ZIRCONIUM CRYSTAL AS A FUNCTION OF TEMPERATURE AND OXYGEN EXPOSURE, EXPANDED SCALE
See legend in Figure 3 for symbols.

The rate at which oxygen accumulates on the surface decreases with increasing temperatures during stages (1) and (3). Stage (2), the slow growth regime, appears to be of negligible duration at 773 K but extends to longer exposure periods at higher temperatures. The final steady-state level of surface coverage attained on the crystal specimen in stage (4) reaches a lower value as the temperature of the specimen increases.

During stage (3), energy shifts in the zirconium AES peaks are observed, indicating the beginning of chemical changes on the surface. As mentioned earlier, these peak shifts are likely due to the formation and growth of a condensed phase of a zirconium oxide. Hence, the uptake of oxygen by a zirconium surface appears to be a sequential process in which initial chemisorption is followed by nucleation and growth of an oxide phase. The experimental curves indicate that formation of the oxide phase is favored by lower temperatures and by higher oxygen pressures. Conversely, the chemisorption regime is extended at higher temperatures and at lower oxygen pressures.

Mass Spectrometric Measurements

The residual oxygen partial pressure in the specimen chamber was monitored concurrently with the AES measurements. Entering oxygen molecules that do not adsorb or react irreversibly on the zirconium specimen surface are pumped out of the chamber. Thus a mass balance in oxygen is described by the following equation:

$$r_{Zr} = \dot{m} - SP_{O_2}$$

where $\dot{m}$ is the mass flow rate of oxygen into the chamber through the capillary tube, r_{Zr} is the rate of oxygen uptake by the zirconium specimen, and S is the pumping speed of the vacuum system for oxygen. In our experiments, $\dot{m}$ is calculated from the observed pressure at the inlet of the capillary tube, the measured conductance of the tube and P_{O_2} , which is monitored by the mass spectrometer. Thus, if S is known, values for r_{Zr} can be calculated. We evaluated pumping speed by measuring

the steady-state oxygen partial pressure in the chamber with the zirconium specimen absent, over a range of values of $\dot{m}$. The pumping speed was found to vary from 600 liters s^{-1} at $\dot{m} = 2.7 \times 10^{-2}$ Pa liters s^{-1} to 900 liters s^{-1} at $\dot{m} = 4 \times 10^{-3}$ Pa liters s^{-1} . The precision of this measurement was relatively poor because S exhibited some dependence on the chamber pressure and also on the immediate history of the system (it increased, for example, when titanium was freshly deposited in the sublimation pump). However over most of the range of pressure variation observed in one kinetic experiment, the pumping speed was found to be reasonably constant ($\pm 25\%$).

The curves shown in Figure 5 illustrate the change in oxygen pressure that occurs during exposure of the zirconium specimen to a constant flux of the gas. The scale on the abscissa in Figure 5 is identical to that in Figure 3, so that changes in P_{O_2} can be compared directly with the amount of oxygen observed on the crystal surface by AES. The oxygen partial pressure in the chamber increases monotonically with increasing exposure until it reaches a steady-state value (Figure 5). There is no discontinuity in the rate of increase of oxygen pressure corresponding to the first plateau in the rate of growth of oxygen on the zirconium surface (compare the respective curves in Figures 3 and 5). This observation, that r_{Zr} exhibits a finite value in a region where the oxygen surface coverage is nearly constant, indicates that oxygen must be diffusing into the crystal as rapidly as it chemisorbs. At longer exposures, both surface coverage and P_{O_2} become constant. Based on our estimated values of S and the measured values of P_{O_2} , oxygen is still diffusing into the zirconium crystal but at a much lower rate. The steady-state rate of oxygen uptake was estimated to vary from $0.7 \pm 0.3 \times 10^{20}$ molec $cm^{-2} s^{-1}$ torr $^{-1}$ at 930 K to $1.6 \pm 0.3 \times 10^{20}$ molec $cm^{-2} s^{-1}$ torr $^{-1}$ at 1050 K with an apparent activation energy of $+9 \pm 4$ kcal mole $^{-1}$. It is this regime, undoubtedly, in which the linear oxygen uptake rates were observed by Nagasaka et al.¹ Where the experimental conditions overlap, our values of oxygen uptake rates are about an order of magnitude greater than these reported by these investigations.

FIGURE 5 VARIATION OF P_{O_2} AS A FUNCTION OF OXYGEN EXPOSURE AT VARIOUS TEMPERATURES

However, within the precision of our measurements and of the estimate of our pumping speed, this agreement is reasonable.

Dissolution of Surface Oxide

After a steady-state P_{O_2} and a constant surface coverage are attained, interruption of the supply of oxygen to the crystal causes the surface oxygen level to gradually decrease. During this surface decay, the oxygen partial pressure in the chamber does not increase, an indication that the surface oxygen is disappearing by diffusion into the bulk of the crystal. The decrease in the normalized surface oxygen AES peak height is plotted as a function of time in Figure 6. It is evident that the rate of diminution in surface oxygen depends on the temperature and on the previous oxygen exposure. After an initial rapid loss of surface oxygen, subsequent loss rates are very slow; that is, approximately 8 hours at 963 K are required to attain a nearly zero oxygen coverage. Note that the extent of surface oxygen coverage attained after the initial rapid loss appears to correspond to the steady-state chemisorption level (stage 2) observed during oxygen exposure. In view of the great affinity of Zr (bulk) for oxygen, the longevity of this oxygen adstate is remarkable.

DISCUSSION

The rate of oxygen surface coverage is proportional to the oxygen exposure, but the rate decreases with increasing temperature. However, the total rate of oxygen uptake calculated from the mass spectrometric data indicates that the total rate increases at higher temperature. The disparate behavior between AES and mass spectrometric data is due to the diffusion of oxygen into the bulk of the zirconium crystal. Zirconium metal can dissolve up to 28.6 atomic percent of oxygen, and the rate of diffusion of oxygen in zirconium metal becomes significant above 773 K.¹³ The initial rate of surface coverage as measured by AES is plotted against inverse temperature in Figure 7, and a negative activation energy of $-44 \text{ kcal mole}^{-1}$ is obtained. Indeed, this value is identical but

SA-5780-23

FIGURE 6 DISSOLUTION OF SURFACE OXYGEN AT VARIOUS TEMPERATURES

FIGURE 7 VARIATION OF INITIAL RATE WITH TEMPERATURE

opposite in sign to the activation energy reported for the diffusion of oxygen in zirconium metal.¹³ The total uptake of oxygen includes both surface accumulation and dissolution in the bulk. Thus, as the temperature increases, the rate of dissolution also increases thereby decreasing the surface coverage at any given oxygen exposure.

Since the rate of diffusion is proportional to the concentration gradient between the surface and the bulk, the diffusive flux would be low at the start of the exposure while oxygen accumulates on the surface. As the coverage increases, the extent of chemisorbed oxygen is determined by the dynamic competition between the adsorption rate of oxygen on the surface and by the rate of diffusion of oxygen into the bulk of the crystal. As the surface sites become filled with oxygen, the chemisorption rate decreases and the total uptake rate is then determined essentially by the rate of diffusion into the crystal.

As the concentration of oxygen in the near surface layers reaches a critical value, the AES oxygen peak height begins to increase. During this growth period, the zirconium Auger peaks shift to lower energy, indicating the formation of a condensed oxide layer. The characteristic shape of the kinetic curves (coverage versus exposure) and the Auger energy shifts, taken together, give strong support to the hypothesis that in this region an oxide layer nucleates and grows. At this stage, the oxygen uptake rate is governed by the rate of the oxide growth and by the rate of diffusion of oxygen into the bulk.

When the surface is covered with the oxide layer, the oxygen uptake rate becomes limited by the diffusion of oxygen through the oxide into the metal. The rate of diffusion of oxygen in the oxide is significantly lower than in the metal,¹⁴ and thus the oxygen uptake rate decreases. In this region (stage 4) both the surface coverage as measured by AES and the uptake rate as calculated from oxygen partial pressure is constant. Even though the precision of the total oxygen uptake measurement is poor in this study, we emphasize that the oxide layer is dynamic and that a steady-state condition exists between the oxygen arrival rate from the gas phase and the rate of diffusion into the crystal. In the absence of gaseous oxygen, the oxide layer dissolves into the metal.

The conditions of temperature and oxygen pressure used in this study overlap those used by Nagasaka et al.¹ Under these conditions an oxide layer would be formed in less than a few minutes. The reported linear oxygen uptake rate at higher exposure suggests that the oxide layer has a nearly constant thickness with steady-state diffusion of oxygen through the oxide governing the rate of oxygen uptake. Similar considerations apply to the data reported by Dechamps and Lehr.² Indeed the existence of a thin oxide layer was postulated earlier by Dechamps and Lehr.² The present AES study confirms the existence of such an oxide layer and permits us to determine its thickness.

At the highest coverage of oxygen recorded in this study the Auger peaks corresponding to metallic zirconium are still evident in the spectra, suggesting that the thickness of the oxide layer is approximately 1 nm (10 Å), the escape depth of Auger electrons with a kinetic energy of 150 eV. The AES oxygen peak height attained during the final steady state condition decreases with increasing temperature (Figure 3); thus, the thickness of the oxide layer could become even smaller as the temperature increases.

According to Nagasaka et al.,² the activation energy associated with the linear oxygen uptake rate is about 10 kcal mole⁻¹, and our results tend to agree with that value. However, this value is rather small in comparison to the activation energy of 56 kcal mole⁻¹ reported for diffusion of oxygen in zirconium oxide.¹⁴ This discrepancy may be due to the nature of the oxide layer formed initially on the metal under the conditions employed. In fact, the activation energy for oxygen diffusion in oxide scales formed on metallic zirconium is substantially lower (~29 kcal mole⁻¹).¹⁴ The initial oxide layer may have a high defect concentration and, according to Kofstad,¹⁵ the oxide may be a p-conductor, a mixed ionic/electronic conductor, or an n-conductor, depending on the stoichiometry and the impurity level. The studies conducted by Bradhurst et al.¹⁶ and by Lightstone and Pemsler¹⁷ have shown that the rate of ionic transport in the oxide is appreciable and that the growth of the oxide layer is controlled by the rate of transport of electronic defects. The

transport of electrons have a rather low activation energy of 2 to 3 kcal mole⁻¹. In a mixed kinetic regime in which ionic and electronic transport controls the oxygen diffusion, the activation energy required may be comparable to the observed value.

An alternative scheme to explain the observed activation energy involves the adsorption of oxygen on the oxide surface and subsequent diffusion. The rate of adsorption decreases with increasing temperature while the rate of diffusion increases. Thus in a mixed kinetic regime, the combined effect of these two rates will result in a modest apparent activation energy as observed.

CONCLUSIONS

The initial stage of oxidation of a clean zirconium surface proceeds first as a chemisorption process followed by nucleation and growth of an oxide layer. At temperatures above 773 K, the rate of diffusion of oxygen into the bulk becomes significant and governs the extent of the chemisorption regime. At higher temperatures, the chemisorption regime extends to long exposure periods, whereas at low temperatures, an oxide is formed rapidly. The observed linear rate of oxygen uptake after the appearance of the surface oxide may be due to diffusion of oxygen through an oxide layer of constant thickness. This oxide layer formed at very low oxygen pressures is estimated to be approximately 1 nm thick.

REFERENCES

1. M. Nagasaka, E. Udeya, and T. Yamashina, Vacuum, **23** (2), 51 (1973).
2. M. Dechamps and P. Lehr, Compr. Rend. Acad. Sci. (Paris), **C270**, 1933 (1970).
3. G. Horz and M. Hammel, J. Nuclear Materials, **55**, 284 (1975).
4. C. C. Chang in Characterization of Solid Surfaces, edited by P. F. Kane and G. B. Larrabee (Plenum Press, New York, 1974), p. 537.
5. T. A. Carlson, Photoelectron and Auger Spectroscopy, (Plenum Press, New York, 1975), p. 264.

6. S. Dushman, Scientific Foundations of Vacuum Techniques (John Wiley and Sons, Inc., U.S.A., 1958, p. 17).
7. Y. E. Strausser and J. J. Uebbing, Chart of Auger Electron Energies (Varian Associates, Palo Alto, 1971).
8. A. M. Horgan and I. Dalins, Surface Sci., 36, (1973).
9. P. H. Holloway, Surface Sci., 54, 506 (1976).
10. J. W. Haas, J. T. Grant, and G. J. Dooley III, J. Appl. Phys., 43, 1853 (1972).
11. G. Ertl and S. Wandelt, Surface Sci., 50, 479 (1975).
12. Y. E. Strausser and J. H. Johannessen, J. Vac. Sci. Technol., 13, 48 (1976).
13. I. G. Ritchie and A. Atrens, J. Nuclear, Materials, 67, 254 (1977).
14. P. Kofstad, Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides, (Wiley Interscience, Inc., U.S.A., 1972), p. 158-159.
15. P. Kofstad, Corrosion NACE, 24, 379 (1961).
16. D. H. Bradhurst, J. E. Draley, and C. J. Van Drunen, J. Electrochem. Soc., 112, 1171 (1965).
17. J. B. Lightstone and J. Pemsler, Symposium on Mass Transport in Oxides, National Bureau of Standards, October 1967, NBS Special Publication 296 (August 1968).

Appendix K

CHEMICAL ASPECTS OF IODINE-INDUCED
STRESS CORROSION CRACKING OF ZIRCALOYS

By

D. Cubicciotti, R. L. Jones, B. C. Syrett

SRI International
Menlo Park, California 94025

ABSTRACT

Crack initiation is believed to be the most time consuming step in the overall process of iodine-induced stress corrosion cracking (SCC) of Zircalloys. We are investigating the chemical aspects of this process. In earlier papers we have presented results concerning the thermodynamics of the Zr-I system. Although four gaseous zirconium iodides were characterized, it was shown that the only gaseous species of importance in SCC was the tetraiodide (ZrI_4). We are determining the thermodynamics of the solid zirconium iodides. There are four distinct solid phases corresponding roughly to the tetra-, tri-, di-, and mono-iodide and a chemisorbed state for iodine on zirconium. The equilibrium gas phase over those solids has partial pressures of ZrI_4 -gas, which decreases as the I/Zr ratio in the solid decreases. Thus gaseous transport of iodine (as ZrI_4) can occur from a higher iodide, formed at the site of first reaction, to lower iodides at other locations and to freshly formed metal surface at a crack tip.

SEM examinations of failure sites in iodine induced SCC has provided evidence that crack initiation sites are frequently associated with

locally high concentrations of alloying additives (i.e., Fe, Cr) or impurities (i.e., Al, Si) in Zircaloy surfaces. Additional evidence of this association will be presented from tube pressurization tests of batches of commercial Zircaloy cladding. The failure sites in these tests had regions containing above average concentrations of iron which were clearly observable in SEM after argon ion milling to remove surface layers of corrosion products. Reactions of gaseous ZrI_4 with Zircaloy surfaces were studied. Regions of greatest reactivity were associated with high local concentrations of Fe. Studies of the rates of reaction of specially prepared Zr-Fe alloys also showed greater reactivity with ZrI_4 than Zr itself.

The mechanism of iodine induced SCC of Zircaloys, in the light of this information, is as follows. Iodine (or ZrI_4) reacts with exposed Zircaloy surfaces to form solid zirconium iodides, which then provide a source of gaseous ZrI_4 . The ZrI_4 , in turn, reacts with the sites in the Zircaloy surface that become available as the metal is strained--most rapidly at sites containing higher than average concentrations of alloying additives--to form embrittled regions in the metal. Those regions fail first under the applied stress and create crack nuclei which propagate under the continuing action of stress and ZrI_4 environment.

CHEMISTRY OF THE ZIRCONIUM-IODINE SYSTEM

The fractography of cracks formed in iodine is very similar to that observed in the PCI failure of Zircaloy clad fuel rods.¹ Recently Wood et al.,² have shown that the strain at failure in an iodine environment is much smaller than in cadmium which suggests that iodine SCC is more relevant to PCI failures than cadmium cracking. We believe that fission product iodine is the aggressive agent in PCI failures¹ and thus it is important to understand the chemistry of the zirconium-iodine system to help clarify the SCC mechanism.

Gaseous Iodides

The enthalpies of formation in the literature for the zirconium iodides, except ZrI_4 , are generally incorrect. They are all based either on estimates or dubious interpretations of experimental results. We have recently used a mass spectrometer method³ to measure the partial pressures of the gaseous iodides in equilibrium with zirconium metal. From those results, the enthalpies of formation of gaseous ZrI_3 , ZrI_2 , and ZrI were derived. The details of the methods used and the results obtained have been reported.³ Table 1 summarizes the thermodynamic data, and Figure 1 gives the partial pressures of the gases in equilibrium with zirconium metal at two different pressures of total iodine-containing species [i.e., $P(\text{total I})$].

For temperatures typical of Zircaloy cladding inner surfaces in LWR operation (~ 650 K), the only important gaseous species containing Zr is ZrI_4 . As $P(\text{total I})$ decreases, the lower iodides become more important relative to ZrI_4 ; however, at 650 K the gases dissociate to iodine before the lower iodides become more important than ZrI_4 . Therefore, any mechanism for iodine-induced SCC of Zircaloy that involves transport of Zr must invoke primarily ZrI_4 .

Table 1

THERMODYNAMIC CONSTANTS FOR GASEOUS ZIRCONIUM IODIDES

Gaseous Species	Standard Enthalpy of Formation at 298 K (kJ/mol)	Standard Free Energy Function* (J/mol)	
		500 K	1000 K
ZrI_4	-355	459	501
ZrI_3	-129	410	442
ZrI_2	+136	354	378
ZrI	+403	280	296

* i.e. - $\frac{\Delta G^\circ(T) - \Delta H_{298}}{T}$

Source: Reference 3.

(a) For $P(\text{total I}) = 10^{-4}$ atm

(b) For $P(\text{total I}) = 10^{-8}$ atm

Figure 1. Partial pressures of gases in equilibrium with solid zirconium.
($P(\text{total I})$ = sum of pressures of iodine species expressed as atomic iodine.)

Solid Iodides

We have studied the thermodynamics of the solid zirconium iodides by vapor pressure measurements. At equilibrium with Zr metal we found the pressure of gaseous ZrI_4 is much larger than those of the lower gaseous iodides (ZrI_3 , ZrI_2 , ZrI). Thermodynamic considerations lead to the conclusion that the vapor in equilibrium with any solid iodides must be even richer in ZrI_4 than in lower iodides. Therefore, the vapor in equilibrium with any solid iodides is essentially ZrI_4 . In our investigations the partial pressures of ZrI_4 in equilibrium with the solid iodides were measured by a torsion-effusion technique. At the same time, the cell was suspended from a microbalance so that the amount of ZrI_4 evaporated is known. Thus, the composition of the solid remaining in the cell can be determined. The method has been described in our work in the thermodynamics of vaporization of ZrI_4 .⁴

The vaporization of gaseous ZrI_4 from solid iodides must be interpreted on the basis of the phase rule. The gas is always ZrI_4 ; therefore, a single condensed phase, the system is bivariant and the pressure depends on the temperature and composition of the solid. For two condensed phases, the system is univariant and the vaporization reaction can be generalized as follows:

Therefore as ZrI_4 is evaporated from a solid that is initially ZrI_{4-x} , the composition of the solid changes and x becomes larger, eventually reaching 4. For a fixed temperature, the pressure of ZrI_4 remains constant when two solids are in equilibrium and decreases in one solid phase regions. Shelton and coworkers⁵ have used this method for part of the Zr-I system. We have studied other regions of the system^{6,7} and have combined Shelton's results with the composition studies of Corbett et al.⁸ Our interpretation of the vaporization results follows.

There are four regions of one phase homogeneous solid solution:

$\text{ZrI}_{4+\delta}$ to $\text{ZrI}_{4-\gamma}$ (δ and γ are as yet unknown)	"tetraiodide"
$\text{ZrI}_{3.4}$ to $\text{ZrI}_{2.8}$	"triiodide"
$\text{ZrI}_{2.1}$ to $\text{ZrI}_{1.9}$	"diiodide"
$\text{ZrI}_{1.3}$ to $\text{ZrI}_{1.1}$	"monoiodide"

The composition limits are probably correct to ± 0.1 . The information about these phases becomes less certain as the iodine content decreases. Between the homogeneous solids are regions in which two solid phases are in equilibrium. Figure 2 presents an isothermal cut of the pressure-composition diagram. The far right side of the diagram is still uncertain. A pressure-temperature diagram is given in Figure 3. The lines represent the pressures of ZrI_4 in the univariant regions (i.e., with two solid phases present). They correspond to the pressures of gaseous ZrI_4 for the following equilibria:

Kinetics of Reaction

Iodine vapor reacts rapidly with clean zirconium metal to form a protective layer of solid iodides on the surface. We have studied the somewhat milder reaction of gaseous ZrI_4 with zirconium surfaces. Samples of Zr sheet and ZrI_4 were sealed into evacuated glass bulbs and heated to 525 K. Thus, the Zr was exposed to about 40 Pa of ZrI_4 vapor. The bulbs were opened in a dry box and the metal sample transferred under dry inert atmosphere to a scanning electron microscope for surface examination.

SA-5780-28

Figure 2. Pressure of ZrI_4 as a function of composition of solid Zr-I phases at 650 K. Dashed lines indicate estimated portions. Lower curve gives enthalpies of vaporization.

Figure 3. Pressures of ZrI_4 in gas in equilibrium with solid zirconium iodide phases. Lines indicate the regions of stability of two solid phases. Compositions of the equilibrium solid iodides are indicated in the figure. The areas between the lines represent solid iodides of variable composition. The shaded area with question marks indicates the probable location of chemisorption curves for iodine on zirconium. The cross indicates the lower iodine concentration at which SCC was observed by Peehs et al. (10).

The first reaction products that formed on the surface were the isolated crystals shown in Figure 4. The surface of the metal between the crystals has a thin layer of iodide. For longer exposure times, the crystals increase in size and also in stoichiometry, reaching a composition of about the monoiodide. When the monoiodide crystals have grown so large that they cover the surface, they become covered by diiodide. Figure 5 shows a surface covered by diiodide of varying stoichiometry. We presume that the regions having different sized crystals correspond to various grains in the substrate metal that have orientations of differing reactivity when exposed to the gas. Figure 6 shows the cross section of a relatively thick surface film of iodides. The film has a layered structure: the large crystals on the top are triiodide, the compact columnar layer is monoiodide; and a thin layer of diiodide appears between the two layers. The diiodide is not readily seen in this figure but can be identified under higher magnification.

A piece of Sandvik Zircaloy-2 tubing was heated in a bulb containing ZrI_4 , as above, and the inner tubing surface was examined in SEM (Figure 7). Before exposure to ZrI_4 the surface had been examined in the SEM, and exhibited the relatively featureless appearance of the chemically etched surfaces shown earlier in Figure 4. Thus, the gravel-like mounds on the surface Figure 7 were the products resulting from corrosion by ZrI_4 at the more reactive surface sites. The larger the mound, the more reactive the original site in the metal surface. A number of those mounds were analyzed in the SEM. The results are given in the figure caption. Each mound exhibited a strong iodine signal and also a distinct signal representing iron (in the range of a few percent of the Zr signal). The least corroded area examined (spot d) had no detectable iodine or iron, which indicates that the sites in the Zircaloy-2 surface that are most reactive to ZrI_4 gas contain some iron.

AMOUNT OF IODINE REQUIRED FOR SCC

Any mechanism for iodine SCC must consider whether iodine plays its role as a gas or as a solid on the surface of the Zircaloy. If gaseous iodine species are involved (either as a gaseous iodide or as iodine

SA-4197-397

Figure 4. SEM photograph of surface of zirconium exposed at 625 K to 100 Pa of gaseous ZrI_4 for 15 minutes. The light gray crystals are the initial stages of formation of ZrI_4 . The darker gray regions were Zr with a trace (surface layer) of I (width of photograph = 20 μm).

SA-4197-398

Figure 5. SEM photograph of surface of zirconium exposed at 625 K to 100 Pa of gaseous ZrI_4 for 24 hours. Analysis of the darker gray crystals showed a ratio of I to Zr of 1.6 to 1.8 while for the light crystals the ratio was 2.3 (width of photograph = 20 μm).

SA-4197-399

Figure 6. SEM photograph of the cross section of a fractured surface layer of iodides formed on zirconium exposed at 775 K to 40 kPa of Gaseous ZrI_4 for 24 hours. Analysis of the crystals on top of the layer showed a ratio of I to Zr of 2.8; the columnar layer of crystals, 1.0; and a thin intermediate layer of 1.8. The zirconium surface in the foreground had a trace of iodine (width of photograph = 50 μm).

SA-4197-400

Figure 7. SEM photograph of inner surface of Zircaloy-2 tubing after exposure at 625 K to 40 Pa ZrI_4 gas for 24 hours. Analyses of sites indicated by lettered arrows showed the following elemental ratios:

	Zr	I	Fe
(a) White mound	1	0.2	0.005
(b) Gray mound	1	0.5	0.02
(c) Gray mound	1	0.5	0.02
(d) Flat surface	1	0	0

(Width of photograph = 0.1 mm)

itself), then the iodine concentration should be expressed on a volumetric basis (i.e., in grams per liter of gas). If however, the mechanism involves a solid iodide, then the concentration should be expressed on an area basis (i.e., as grams per unit area of Zircaloy surface).

Cox and Wood⁹ reviewed the available information in 1974 but did not discuss whether iodine concentration was more properly expressed by volume or area. They indicated that for short times (< 60 h) the critical concentration for the occurrence of SCC was $\sim 1-5 \times 10^{-4}$ g/ml of gas phase; however, for long times (200 to 1,000 h), cracking of split-ring samples was observed at concentrations as low as 3×10^{-6} g/ml, which is equivalent to a concentration of 1.5×10^{-5} g/cm² of Zircaloy surface.

More recently Peehs et al.¹⁰ reported on the influence of iodine concentration on SCC of Zircaloy. Their results are in accord with a mechanism involving formation of solid surface iodides on the Zircaloy and not with a mechanism involving gaseous iodides. In particular, they found that when they released small amounts of iodine (< 10^{-3} g/cm²) near a stressed Zircaloy surface, microcracks initiated in "islands"; these islands suggest a nonuniformly distributed condensate layer. In addition, they found that release of small amounts of iodine near a stressed flaw would cause SCC, but, if released far from the flaw, it would not. Both these observations indicate that solid iodides on the Zircaloy surface cause SCC. If gaseous iodides were the primary active species, they would be transported evenly and fairly rapidly over the Zircaloy surface and the resulting cracking would be less localized.

Peehs et al.¹⁰ also compared the minimum amounts of iodine required to cause cracking with the thermodynamics of the Zr-I system and concluded that SCC occurred only when a solid iodide was present. The thermodynamic data they used from the literature were incorrect, but we find their conclusions to be substantially correct. The cross in Figure 3 indicates the lowest effective concentration of iodine ($\approx 10^{-5}$ moles/l) at which SCC was observed. The figure indicates that if iodine at those concentrations were introduced into a Zircaloy container, it would form solid iodides on the metal surface and leave only a negligible amount of iodine

($\sim 10^{-10}$ atm) in the gas (as ZrI_4). This result agrees with the observations of Peehs et al.¹⁰ that the gaseous iodides are converted to solid iodides to effect SCC. Our results show this not to be the case because solid iodides form when the concentrations of gaseous iodides are much lower.

In short, these observations indicate that solid iodides on the Zircaloy surfaces are involved in SCC. The minimum surface concentration that caused SCC in the test of Peehs et al.¹⁰ ($\sim 1 \times 10^{-6}$ g iodine per square centimeter of Zircaloy) was smaller than the value given by Cox and Wood⁹ (1.5×10^{-5} g/cm²). If the surface were atomically flat and the iodine atoms were distributed uniformly, Peehs' value would represent about 5×10^{15} atoms of iodine per square centimeter or about 10 monolayers of iodine on the surface (assuming $20 \text{ \AA}^2$ per iodine atom).

Actually, some areas are much more reactive than others, and the minimum amount of iodine on the active surface area that could cause SCC is probably much greater. We suspect these active areas may be the same as the chemically inhomogeneous regions to be discussed below.

RELATION TO INTERNAL FUEL ROD CHEMISTRY

The availability of iodine for SCC of reactor fuel rods is constrained in two ways. First, iodine like all other volatile fission products, is trapped in the fuel (UO_2) matrix as it is formed and does not come in contact with the cladding until it is released from the fuel. Second, to react with zirconium or Zircaloy, the partial pressure of the available iodine must be greater than the equilibrium iodine pressure in the system (zirconium + lowest iodide). This last concept will be discussed first.

The relevant equilibrium iodine pressure can be evaluated as follows. Figure 3 indicates that when solid Zr and $\text{ZrI}_{1.1}$ are in equilibrium at 600 K the ZrI_4 pressure is about 10^{-9} atm. Thus, for the reaction $2.6 \text{ Zr(s)} + \text{ZrI}_4(\text{g}) = 3.6 \text{ ZrI}_{1.1}(\text{s})$ the standard free energy change is

$$\Delta G^\circ = +RT \ln p (\text{ZrI}_4) = -25 \text{ kcal/mole} \quad (6)$$

The standard free energy for formation of gaseous ZrI_4 (i.e., for the reaction at 600 K)

is $\Delta G^\circ = -98.6$ kcal. Therefore, for the reaction

the standard free energy change is -74 kcal and the partial pressure of iodine in equilibrium with Zr and $\text{ZrI}_{1.1}$ is $10^{-12.4}$ atm at 600 K. A similar chain of logic leads to the result that the iodine pressure required to form chemisorbed iodide on zirconium is estimated to be $\sim 10^{-16}$ atm at 600 K (if the crosshatched area in Figure 3 represents the chemisorbed state).

An evaluation of fuel rod chemistry¹¹ indicates that after some release of fission products from the fuel, the relevant substances in contact with the cladding are deposits of CsI crystals, cesium vapor at pressures of the order of 10^{-2} atm, and UO_2 itself. The equilibrium iodine pressure in the fuel-cladding gap is established by the reaction

The equilibrium iodine partial pressure is determined by the oxygen potential of the fuel. From reasonable estimates of this quantity¹² and of the standard free energy of the reaction, one estimates that the equilibrium partial pressure of iodine is of the order of 10^{-30} atm at 600 K, which is clearly too small to react with zirconium and cause SCC. Thus, radiolysis of CsI by energetic particles or photons is necessary for SCC. We have shown that gamma photons can release iodine,¹³ and we presume that energetic particles can also release iodine.

Thus, we believe that crystals of CsI deposited on the inner cladding surface act as sources of iodine, which is released by radiolysis from the CsI. The iodine reacts with the Zircaloy surface immediately beneath the deposit in areas where the amounts of iodine that could be transferred from a CsI deposit to the cladding surface in a fuel rod

are estimated¹ to be substantially greater than the minimum values measured in laboratory tests. A schematic representation of the transfer process is shown in Figure 8.

CHEMICAL INHOMOGENEITIES IN ZIRCALOY TUBING

Association of Failure Sites with Chemical Inhomogeneities

There is an increasing amount of evidence¹⁴ that crack initiation sites are associated with local higher-than-normal concentrations of certain alloying additives (Fe, Cr, Ni) or impurities (Al, Si, other), which we have chosen to call "chemical inhomogeneities." Iron seems to be encountered particularly frequently. In Reference¹⁵ we reported several instances of the association of cracks with regions containing Fe (Figures 10, 11, 14, 15, 18, and 21). In another report¹⁶ we have found several examples in which the brittle failure cracks formed in tube pressurization tests were associated with chemical inhomogeneities. The identification of the causes of crack nucleation was not an objective of the present work, and therefore very little examination of failure sites was performed.

In Section 2 of Reference 16 failures of both supplier's tubing were associated with chemical inhomogeneities containing Fe in the two cases examined. In the tubing less resistant to SCC, the more extensive inhomogeneities could have caused the poorer SCC resistance. In the tests described in the Appendix of Reference 16, moreover, all of the failures that were not too badly deformed were found to be associated with locally high Fe concentrations. It should be noted that in the studies described in the Appendix of Reference 16, we found the most resistant tubing to iodine induced SCC of any batch we have tested.

There is a good indication therefore, that crack initiation occurs at chemical inhomogeneities. It is possible that the size and chemical reactivity of the inhomogeneities are major factors in determining the SCC susceptibility of a sample of tubing.

TA-350543-85

Figure 8. Schematic representation of transfer of iodine from CsI to form zirconium iodides on cladding inner surfaces. Iodine is released from the CsI by radiolysis in regions beneath the deposits of fission products where Cs vapor cannot readily arrive. The iodine is thus available to react with the Zr and result in SCC.

Distribution of Chemical Inhomogeneities in Commercial Tubing

As part of our continuing assessment of commercial Zircaloy claddings used in EPRI programs, we selected three Zircaloy tubings and determined the distribution of the types of chemical inhomogeneity that we have previously found associated with iodine-induced crack initiation.¹⁴⁻¹⁵ Pieces of stress-relieved Zircaloy-4 (7FD11), annealed Zircaloy-2 (7AH11-S), and stress-relieved Zircaloy-2 (7AH11-H) tubing were cut axially so that both the tubing inner surface and the tubing thickness could be examined. These tubings were fully characterized.¹⁵ The cut surfaces were ground with 600 grit silicon carbide paper, and then the longitudinal and the ID surfaces were argon-ion milled and examined in a scanning electron microscope (SEM). The chemical inhomogeneities are less rapidly removed than the matrix metal during ion milling, so the inhomogeneities become small mounds protruding from the Zircaloy surface (Figure 9).

The frequency of occurrence of inhomogeneities in stress-relieved Zircaloy-4 tubing (7FD11) was about the same on the inner surface as it was on the through-wall surface (Table 2). In contrast, in two samples of stress-relieved Zircaloy-2 tubing (7AH11-H), the frequency was higher on the inner surface than on the throughwall surface, considerably so in sample T-48 (Table 2).

Table 2

FREQUENCY OF OCCURRENCE OF MOUNDS OF INHOMOGENEITY IN ZIRCALOY TUBING SAMPLES

Sample	Frequency of Mounds (number per mm ² of surface examined)	
	Inner Surface of Tubing	Through-Wall (i.e., on Cut Surface)
Zircaloy-4 (7FD11)	~ 30	~ 30
Zircaloy-2 (7AH11-H)		
Sample T-48*	~ 4,000	~ 20
Sample T-54*	~ 100	~ 50

* Sample numbers refer to indenter test numbers.¹⁵

(a) INNER SURFACE (width of photograph = 1 mm)

(b) AXIAL SECTION OF TUBE WALL
(width of photograph = 1 mm)

SA-4197-355

Figure 9. SEM photographs of chemical inhomogeneities
in stress-relieved Zircaloy 2 (7AH11-H).

Sample is from Test T-54, ion milled 2 h.

The chemical inhomogeneities on the surfaces of stress-relieved Zircaloy-2 were readily observed, as shown in Figure 9. Most of the mounds were roughly spherical, ranging in diameter from about 5 μm to 50 μm . Occasionally, long narrow particles ($\sim 100 \mu\text{m} \times 10 \mu\text{m}$) were observed, but at a rate of less than one particle per mm^2 of surface. The chemical inhomogeneities (mounds) on the surfaces of annealed Zircaloy-2 (7AH11-S), on the other hand, were much more difficult to discern than those in the equivalent stress-relieved alloy (7AH11-H). The grain structure was well-defined in the annealed material, and after ion etching, the surface was so rough that only large mounds ($> 50 \mu\text{m}$) were evident. Smaller mounds, typical of those shown in Figure 9, were observed with difficulty under high magnification (see Figure 10) but their frequency could not be estimated.

Elemental chemical analyses of the mounds were performed in the SEM by energy- and wavelength-dispersive-X-ray analysis techniques, which were able to detect all elements of atomic number greater than 5. The mounds in all samples were similar and were composed largely of Zr, but they always contained a few percent of one or more of the elements Si, Al, Ti, O, C, Fe, Cr, and Sn, in amounts that were greater, to a varying degree, than those in the nearby matrix metal. A typical analysis of a mound was Zr with 1.1% Si, 0.7% Fe, 0.6% Al, and 0.3% Cr. There was no apparent correlation between the size of the mounds and their chemistry. Pieces of grit containing Si or Al, presumably SiC, SiO₂, or Al₂O₃, were occasionally embedded in the surface. However, they were readily distinguishable from the chemical inhomogeneities in the alloy because they were not intimately incorporated into the Zircaloy surface.

These examinations show that the frequency of occurrence of the chemical inhomogeneities is quite variable. We suspect that the frequency varies markedly from one region to another within the same length of tubing, as evidenced by the variable SCC susceptibilities observed in indenter tests on these and other materials.¹⁵

(width of photograph = 50 μm)

SA-4197-356

Figure 10. SEM photograph of a chemical inhomogeneity on the sectioned surface of the tube wall of a sample of annealed Zircaloy 2 (7AH11-S).

Sample was ion milled 2 h. Analysis of the materials in the inclusions showed Zr with a few percent Fe, Cr, Si, and Al.

Potential Origins of Chemical Inhomogeneities

The frequency of occurrence of the chemical inhomogeneities on the inner tubing surface of one sample (T-48) was larger than the through-wall frequency. This difference indicates that tube forming processes contributed to the population at the inner tube surface. The chemical analyses of most particles showed they contained mainly Zr plus a few percent of one or more other elements. We believe that the large Zr content in these particles indicates that the inhomogeneities formed while the metal was hot enough for interdiffusion to occur or that they had some opportunity to become at least partially incorporated into the surface possibly during a heat treatment operation after they became embedded during a cold working operation.

MECHANISM OF SCC OF ZIRCALOYS

The mechanism of iodine induced stress corrosion cracking (SCC) of Zircaloy tubing was discussed in Section 7 of our earlier work.¹⁵ The model discussed there contained four stages:

- (1) Oxide penetration
- (2) Crack formation
- (3) Crack propagation
- (4) Cladding rupture,

which are illustrated in Figure 11.

This report provides additional data about the influence of a number of variables on the overall time to failure--that is, the time to completion of all four stages. Most of the time to failure has been shown (see Section 6 and Reference 10) to be involved in crack initiation (Stage 2, and possibly Stage 1). Crack initiation is the most important part of the overall SCC process.

Our view of crack initiation follows. The aggressive component of the environment (iodine) attacks the Zircaloy surface wherever it is not protected by a thick coherent oxide (e.g., at a strain-induced crack

SA-4197-195

Figure 11. Micrographs illustrating the four states of iodine-induced cladding failure.

site). This chemical reaction produces solid zirconium iodides, ZrI and possibly ZrI_2 . The solid zirconium iodide produces a small pressure of gaseous ZrI_4 (see Figures 2 and 3 for quantitative estimate). The gaseous ZrI_4 is then available to react with the regions of the Zircaloy surface that contain chemical inhomogeneities (Figure 7 shows areas containing Fe are more chemically reactive).

We suspect that reaction of gaseous ZrI_4 with a region of zirconium containing higher than average Fe causes the iodine to become incorporated into the bulk chemically inhomogeneous volume. The material in the surface produces a local defect that cracks under the applied stress. Gaseous zirconium iodide can diffuse to the root of that crack and react with the freshly-exposed zirconium surface. That reaction can occur because chemisorption of ZrI_4 on clean Zr occurs at a lower partial pressure of gaseous ZrI_4 than that produced by ZrI at the tubing inner surface (Figure 2). Crack propagation then presumably proceeds by iodide-assisted fracture at the crack-tip.

Thus we believe the evidence shows that the most reactive sites in Zircaloy surfaces contain locally higher-than normal concentrations of alloying additives (Fe, sometimes Cr) and impurities (Al, Si possibly others). We propose that the size and nature of those sites determine the degree of susceptibility of the Zircaloy to iodine SCC-Zircaloys containing the largest reactive sites at the surface are the most susceptible. As the size and reactivity of the impurity sites decreases, the susceptibility to SCC decreases.

ACKNOWLEDGMENTS

This research was funded in part by the Electric Power Research Institute under Contract RP 455-1-6 and in part by the U. S. Department of Energy, Division of Basic Energy Sciences under Contract EY-76-S-03-1339.

REFERENCES

1. J.T.A. Roberts, et al., "An SCC Model for Pellet-Cladding Interaction Failures in LWR Fuel Rods," Zirconium in the Nuclear Industry, ASTM STP 681, p. 285, ASTM, Philadelphia, PA, 1979.
2. J. C. Wood, D. G. Hardy, and A. S. Bain, "Mechanistic Studies of Power Ramping Defects and Remedies," ANS Topical Meeting on Light Water Reactor Fuel Performance, Portland, Oregon, American Nuclear Society, Hinsdale, Ill. (1979).
3. P. D. Kleinschmidt, D. Cubicciotti, D. L. Hildenbrand, J. Electrochem. Soc., 125, 1543 (1978).
4. D. Cubicciotti, K. H. Lau, M. J. Ferrante, J. Electrochem. Soc., 125, 972 (1978).
5. M. A. Bhatti, D. B. Copley, R.A.J. Shelton, J. Less Common Metals 55, 293 (1977).
6. D. Cubicciotti, K. H. Lau, "Thermodynamics of Vaporization of ZrI_4 From Substoichiometric Solid Zirconium Iodides," J. Electrochem. Soc. 127, 771 (1979).
7. D. Cubicciotti, K. H. Lau, "Thermodynamics of Vaporization of ZrI_4 in Univariant Region: Zirconium Monoiodide/Zirconium." to be published.
8. J. D. Corbett, et al., J. Am. Chem. Soc. 100, 652 (1978).
9. B. Cox and J. C. Wood, "Iodine Induced Cracking of Zircaloy Fuel Cladding," in Corrosion Problems in Energy Conversion and Generation, C. S. Tedmon, Jr., Ed., The Electrochemical Society, Princeton, N. J., p. 275 (1974).
10. M. Peehs, H. Stehle, E. Steinberg, "Out-of-Pile Testing of Iodine Stress Corrosion Cracking in Zircaloy Tubing Under the Aspect of the PCI-Phenomenon," in Zirconium in the Nuclear Industry, ASTM STP 381, p. 244, ASTM, Philadelphia, PA. 1979.
11. D. Cubicciotti and J. E. Sanecki, J. Nuclear Materials 78, 96 (1978).
12. M. G. Adamson, E. S. Darlin, and J. H. Davies, "Thermomigration and Reactions of Mobile/Active Fission Product Species in LWR Fuel Systems," in Specialists Meeting on Internal Fuel Rod Chemistry, Erlangen, German, International Atomic Energy Agency, Vienna, Austria, (1979).

13. D. Cubicciotti and J. H. Davies, Nucl. Sci. Eng., 60, 314 (1976).
14. D. Cubicciotti, S. M. Howard, and R. L. Jones, J. Nuclear Materials 78, 2 (1978).
15. D. Cubicciotti and R. L. Jones, "EPRI-NASA Cooperative Project on Stress Corrosion Cracking of Zircalloys," EPRI-NP-717, Electric Power Research Institute, Palo Alto, California (1978).
16. D. Cubicciotti, R. L. Jones and B. C. Syrett, "Stress Corrosion Cracking of Zircalloys," EPRI-NP-1329 Electric Power Research Institute, Palo Alto, California (1979).