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CORROSION OF $U_xZr_{1-x}C_{1-y}$ NUCLEAR FUEL MATERIALS IN HYDROGEN GAS AT HIGH PRESSURES AND TEMPERATURES

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Abstract

This paper describes the thermodynamics and kinetics of the corrosion of $U_xZr_{1-x}C_{1-y}$ in hydrogen gas. It describes how corrosion rates are influenced by variables such as pressure, temperature, and gas flow rate. A model is developed which agrees with experimental steady state corrosion rates at 1 atm between 2670 and 3160 K. Under these conditions the corrosion flux is rate limited by the vapor phase transport of Zr(g) away from the solid surface to the bulk gas stream where the partial pressure of Zr(g) is determined by the congruently vaporizing surface composition. Extrapolation of the model to higher pressures indicates that Zr(g) transport should also be rate limiting at higher pressures but the corrosion rate should decrease with increased total pressure due to reduced gaseous diffusion rates. The model predicts that the corrosion rate will increase as the square root of gas velocity for a given temperature and pressure. Calculations demonstrating the effects of gas velocity are in agreement with experimental studies. The addition of hydrocarbons to the hydrogen gas stream is predicted to decrease the corrosion rates significantly.

Introduction

The corrosion behavior of nuclear fuel materials in hot hydrogen is a critical issue for a variety of nuclear propulsion concepts for missions to Mars. In order to maximize the rocket performance certain reactor designs presume operating temperatures in excess of 2800 K in a high velocity flow of high pressure, gaseous hydrogen. For this reason $U_xZr_{1-x}C_{1-y}$ solid solutions are a prime candidate for such applications¹ due to their high melting point, good nuclear properties, and

relatively good resistance to corrosion by hydrogen. Because the rate of corrosion will limit the reactor life, it is important to have a thorough understanding of the corrosion kinetics of $U_xZr_{1-x}C_{1-y}$ materials in hydrogen under a variety of possible operating conditions. The development of models which can account for changes in the many possible operating variables is therefore critical.

The Thermodynamics of Corrosion of Carbide Fuels and the Congruently Vaporizing Surface Composition

During the corrosion of $U_xZr_{1-x}C_{1-y}$ in hot hydrogen, U(g), Zr(g), and hydrocarbons are the predominant product gases. As shown in figure 1, U(g), and hydrocarbons have higher partial pressures than Zr(g), based on thermodynamic calculations. Due largely to its relatively small size, carbon can diffuse rapidly in the $U_xZr_{1-x}C_{1-y}$ rock salt structure. As a consequence of the rapid diffusion of carbon and the high partial pressures of uranium and hydrocarbons relative to zirconium, the surface composition of $U_xZr_{1-x}C_{1-y}$ shifts toward what is referred to as the congruently vaporizing surface composition or CVC.² In accordance with Le Chatelier's principal, the surface composition shifts in such a way as to reduce the total system free energy. As a consequence, the vapor pressures above the CVC are less than those above the starting composition. Because the $U_xZr_{1-x}C_{1-y}$ solid solution has a relatively wide solution range, the CVC can shift markedly from that of the starting composition and, correspondingly, vapor pressures will change significantly. Therefore, it is important to know the CVC for a given set of conditions in order to accurately

determine equilibrium vapor pressures during steady state corrosion. Figure 2 shows the CVC above $U_{.05}Zr_{.95}C_{1.07}$ when exposed to 1 atm of hydrogen at 2000 to 3200 K. Note that in this work the CVCs were calculated using the methods previously described by Storms.²

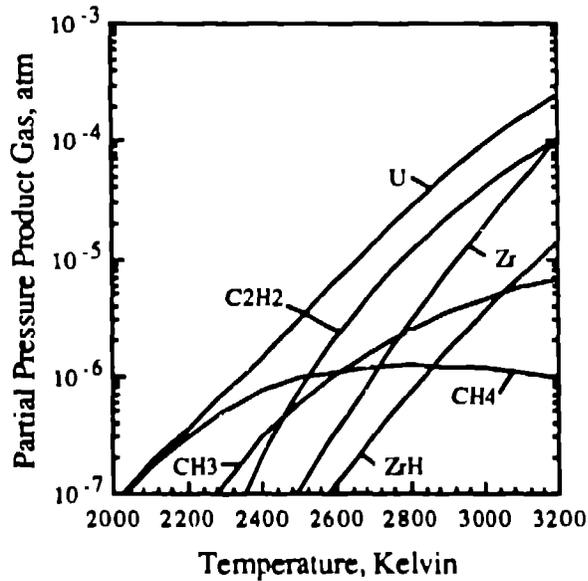


Figure 1. Calculated equilibrium partial pressures above $U_{.05}Zr_{.95}C_{1.07}$ in 1 atm of hydrogen at 2000-3200 K. These represent the partial pressures above $U_{.05}Zr_{.95}C_{1.07}$, before the CVC has developed.

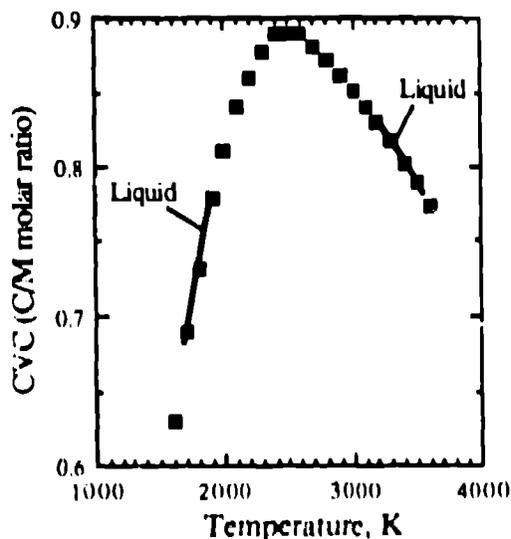


Figure 2. Calculated CVC versus temperature for $U_{.05}Zr_{.95}C_{1.07}$ exposed to 1 atm of hydrogen.

Calculations of Corrosion Rates

The corrosion rate of $U_xZr_{1-x}C_{1-y}$ may be described using a flux equation, analogous to Fick's first law of diffusion, as follows:

$$J_{UZrC} = J_i = -\frac{h_i \Delta p_i}{RT} \quad (1)$$

where J_{UZrC} is the molar flux of $U_xZr_{1-x}C_{1-y}$ away from the surface, J_i is the molar flux of the rate controlling gaseous product species, i , away from the surface, Δp_i is the change in the partial pressure of species i between the bulk gas stream and the CVC surface, and RT has its usual meaning. The average or effective mass transfer coefficient, h_i , may be determined from boundary layer theory and, for the particular bullet-shaped geometry² used in these studies, may be expressed as follows under laminar flow conditions:³

$$h_i = \frac{D_{ij}}{L} (0.70 Re^{1/2} Sc^{1/3}) \quad (2)$$

where L is the characteristic dimension of the solid (bullet diameter), D_{ij} is the gaseous interdiffusion coefficient for species i through, in this case, hydrogen, Re is the Reynolds number, and Sc is the Schmidt coefficient. The gaseous interdiffusion coefficient may be expressed as follows:⁴

$$D_{ij} = \frac{3kT}{8P} \sqrt{\frac{kT}{2P} \left(\frac{m_i + m_j}{m_i m_j} \right)} \cdot \frac{1}{\sigma_{ij}^2 \Omega_D \left(\frac{kT}{\epsilon_{ij}} \right)} \quad (3)$$

where k is the Boltzmann's constant, P is total pressure, and m represents molecular mass. The terms σ and ϵ are Lennard-Jones potential parameters (collision diameter and interaction energy parameter, respectively) and Ω_D is referred to as the Lennard-Jones potential; Values of or methods for calculating these parameters are well documented.^{5,6} The dimensionless terms

R_e and S_c in (2) may be calculated from the following relationships:

$$R_e = \frac{Lv}{\nu} = \frac{\rho v L}{\eta} \quad (4)$$

and

$$S_c = \frac{v}{D_{i-mix}} = \frac{\eta}{\rho D_{i-mix}} \quad (5)$$

where v is the bulk gas stream velocity v is the kinematic gas viscosity, η is the dynamic viscosity, and ρ is the gas density. The monomolecular dynamic viscosities were calculated using the equation:⁶

$$\eta_i = \frac{5}{16} \cdot \frac{\sqrt{\pi m k T}}{(\pi \sigma^2) \cdot \Omega_D (kT/\epsilon)} \quad (6)$$

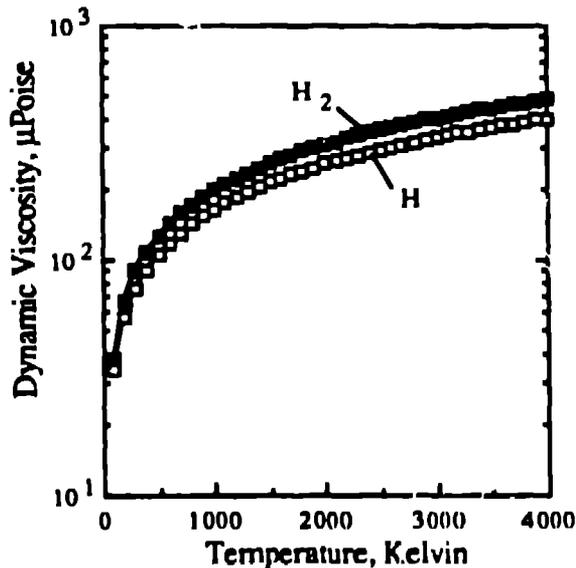


Figure 3. Calculated dynamic viscosity of H and H₂ gas as a function of temperature.

In determining the gas viscosity it is important to consider both molecular and dissociated hydrogen since these species have different individual gas viscosities (see figure 3). In the case of the binary mixture

H-H₂, the dynamic gas viscosity, η_{mix} , was calculated using the following mixture rule:⁵

$$\eta_{mix} = \frac{\sum_{i=1}^N \sqrt{M_i} y_i \eta_i}{\sum_{i=1}^N \sqrt{M_i} y_i} \quad (7)$$

where M is molecular weight and y is the volume fraction of gas species i . In these studies, the concentrations of H and H₂ were assumed to be near equilibrium since the time for dissociation/recombination at these temperatures and pressures is on the order of 10 to 100 milliseconds, as illustrated in figure 4.⁷

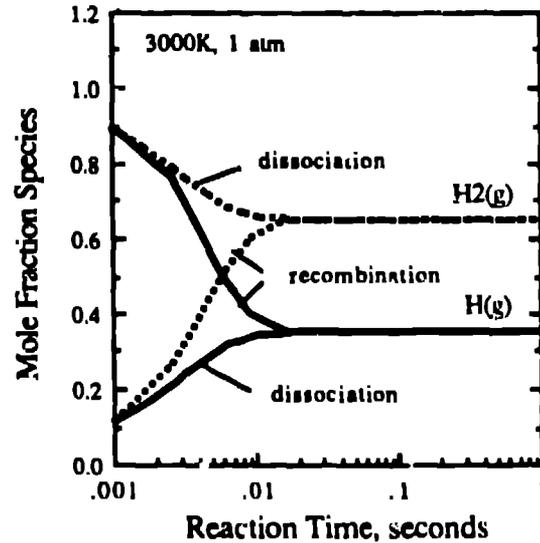


Figure 4. Calculated H and H₂ concentration at 3000 K, 1 atm, shown as a function of both dissociation and recombination reaction time.

Equation (1) was used to calculate the corrosion rate of $U_x Zr_{1-x} C_{1-y}$ in hydrogen at 1 atm between 2500 and 3200K. The values for Δp_i were obtained by calculating the partial pressures above the CVC using thermodynamic data from several sources.⁷⁻¹⁰ In a fast flowing gas stream $\Delta p_i = p_i$ where p_i is the equilibrium partial pressure of the rate limiting gaseous species. Thus the values of Δp_i used in calculating the corrosion fluxes corresponded to the

equilibrium partial pressures of the most stable gaseous products, for example, $U(g)$, $Zr(g)$, $C_2H_2(g)$, and $CH_4(g)$, as shown in figure 1. Because it is well known that solid solutions of UC and ZrC deviate only slightly from Vegard's law, the $U_xZr_{1-x}C_{1-y}$ solid solutions were assumed to be ideal solutions of UC and ZrC_x where thermodynamic data for ZrC_x were determined from activity measurements.¹⁰

Comparison of Calculated and Experimental Corrosion Rates and Extrapolations

Calculated corrosion rates were compared to hydrogen corrosion data from studies performed at Los Alamos National Laboratory which yielded the following Arrhenius relationship for $U_{0.05}Zr_{0.95}C_{1.07}$ in 1 atm of hydrogen at 2670-3190K at a Reynolds number of approximately 500:¹¹

$$\ln \text{rate}(\text{g}/\text{cm}^2\text{-sec}) = 10.891 - \frac{68618}{T} \quad (7)$$

Figure 5 shows a comparison of calculated versus experimental corrosion rates. The calculated data shown in figure 5 are based on two different assumptions: (1) $Zr(g)$ transport from the CVC was rate limiting, and (2) $C_2H_2(g)$ transport from the CVC was rate limiting. These two assumptions gave the best agreement between the model and the data. The relatively good agreement between the experimental data and assumption (1) above suggests that the corrosion of $U_xZr_{1-x}C_{1-y}$ in hydrogen may be rate limited or partially rate limited by gaseous transport of $Zr(g)$ away from the surface.

The model was used to extrapolate to higher pressures as shown in figure 6. Throughout the pressure range shown, the corrosion rate is predicted to be controlled by the rate at which $Zr(g)$ can diffuse through the gaseous boundary layer. Based on these calculations, it is expected that there will be a slight decrease in the corrosion rate as the pressure is increased due to the decreased gaseous diffusion rate of $Zr(g)$. Note also that at very high pressures (>100

atm) liquid is predicted to form on the surface due to the shift in the CVC.

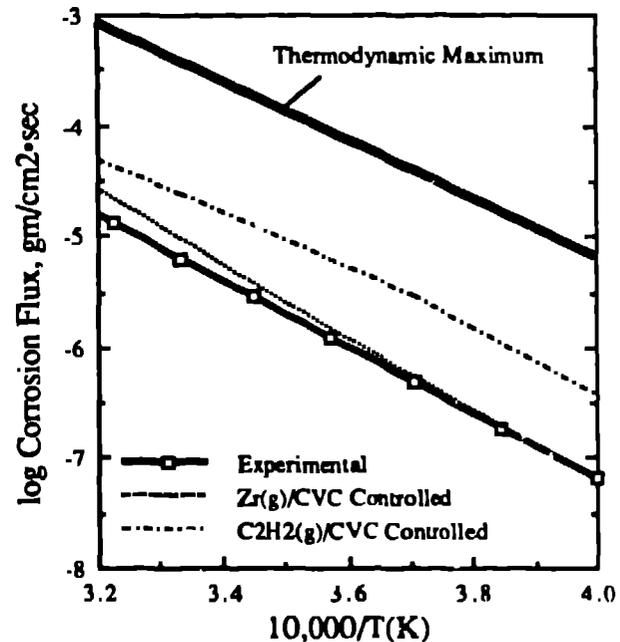


Figure 5. Arrhenius plot of calculated and experimental steady state corrosion rates above the CVC composition of $U_{0.05}Zr_{0.95}C_{1.07}$ in 1 atm of hydrogen.

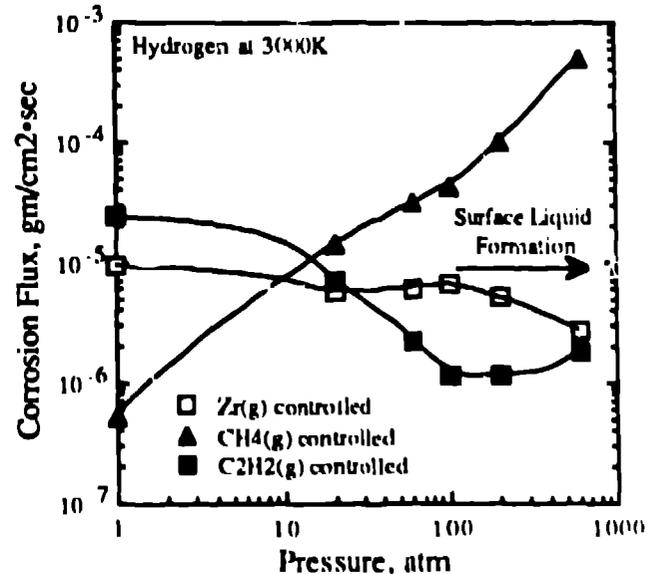


Figure 6. Calculated steady state corrosion rates above the CVC composition of $U_{0.05}Zr_{0.95}C_{1.07}$ in 1-600 atm of hydrogen at 3000 K.

As is apparent from equations (1) and (2), the corrosion flux is a strong function of the bulk gas stream velocity. Because h_i is proportional to the square root to the Reynolds number equation (1) predicts that the corrosion flux increases proportionally with the square root of gas velocity. By plotting the log of the corrosion flux versus the log of the gas velocity a slope of ≈ 0.5 should be observed. Figure 7 shows the effect of gas velocity on the calculated and experimental corrosion rates at 2600 K in 1 atm of hydrogen. Although the slope for the experimental data is less than 0.5, there is a positive correlation between flux and velocity, and there is relatively good agreement between the calculated and experimental values. The fact that the experimental corrosion flux was found to depend on velocity suggests that the underlying assumption of this model (*i.e.*, that the corrosion rate is controlled by gaseous diffusion) is valid since surface reaction rate limited processes are independent of gas velocity. Note that at very high gas velocities the model predicts that the corrosion rate exceeds the thermodynamic maximum (see figure 5) which is not possible. In reality the rate of corrosion approaches the thermodynamic maximum asymptotically at very high gas velocities. Also, at 1 atm and 2600 K, the onset of turbulent flow begins at approximately $1 \cdot 10^5$ cm/sec and the mass transfer coefficient described by equation 2 is no longer applicable.

Summary

A thermokinetic model was developed which accurately characterizes the kinetics of corrosion of $U_xZr_{1-x}C_y$ nuclear fuel materials in hydrogen gas at 1 atm, 2670 to 3100 K. The model indicated that the corrosion rate should increase as a function of the square root of the bulk gas stream velocity. It was predicted that the corrosion rate should decrease slightly as the total system pressure is increased due to the decreased gaseous diffusion rates of the reaction product gases. And it was predicted that the rate of corrosion can be reduced by adding small additions of

hydrocarbons, such as CH_4 , to the H_2 gas stream.

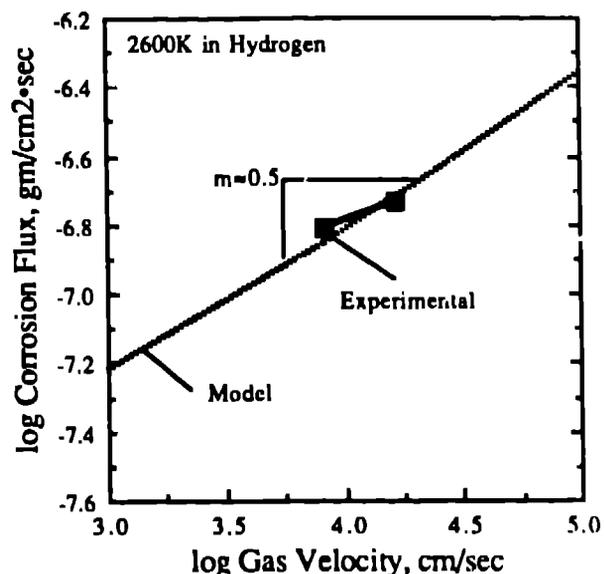


Figure 7. Calculated and experimental steady state corrosion rates plotted as a function of bulk gas stream velocity at 2600 K in 1 atm of hydrogen.

Acknowledgements

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