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TITLE: VAPORIZATION BEHAVIOR OF $U_xZr_{1-x}C_{1-y}$ NUCLEAR FUEL MATERIALS IN HYDROGEN AT HIGH PRESSURES AND TEMPERATURES

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Vaporization Behavior of $U_xZr_{1-x}C_{1-y}$ Nuclear Fuel Materials in Hydrogen at High Pressures and Temperatures

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The corrosion behavior of nuclear fuel materials, such as refractory carbides, in hydrogen gas is an important issue for a variety of space propulsion concepts. The rate of vaporization will limit the reactor life and must therefore be well understood. This paper describes the thermodynamics and kinetics of the vaporization of $U_xZr_{1-x}C_{1-y}$ solid solutions in hydrogen gas; and it describes how vaporization rates are influenced by pressure, temperature, gas flow rate, dissociated hydrogen, and the addition of hydrocarbon to the hydrogen gas stream. It is demonstrated that a thermokinetic model agrees with hydrogen corrosion data at 1 atm between 2670 and 3100K. Comparison of experimental and calculated corrosion fluxes indicates that under these conditions the steady state corrosion of $U_xZr_{1-x}C_{1-y}$ is rate limited by gaseous transport of Zr(g) from the solid surface to the bulk gas stream where the partial pressure of Zr(g) is controlled by the congruently vaporizing surface composition (CVC). 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.* This work extends a model previously described by Storms[1] which was based on experimental data in which he assumed an average vaporization coefficient and Langmuir vaporization. Storms also described the mechanism of formation of the CVC and its importance in determining corrosion rates.

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:

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

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 geometry used in these studies may be expressed as:[2]

$$h_i = \frac{D_{ij}}{L}(0.70\, R_e{}^{1/2} S_c{}^{1/3}) \qquad (2)$$

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, R_e is the Reynolds number, and S_c is the Schmidt coefficient. The gaseous interdiffusion coefficient may be expressed as follows:[3]

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* Calculations suggest that corrosion rates could increase slightly at high pressures due to the formation of ZrH(g). However, good thermodynamic data for this species do not exist.

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

where k is the Boltzmann's constant, P is total pressure, and m represents molecular mass. The terms σ_{ij} and ε_{ij} are Lennard-Jones potential parameters and Ω_D is referred to as the Lennard-Jones potential; Values of or methods for calculating these parameters are well documented.[4,5] The dimensionless terms R_e and S_c in (2) may be calculated from the following relationships:

$$R_e = \frac{Lv}{v} \qquad (4)$$

and

$$S_c = \frac{v}{D_{i\text{-mix}}} \qquad (5)$$

where v is the bulk gas stream velocity and v is the kinematic viscosity.

Equation (1) was used to calculate the corrosion rate of $U_xZr_{1-x}C_{1-y}$ 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.[6-9] In a fast flowing gas stream $\Delta p_i \approx p_i$ 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 possibly ZrH(g). 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.[9]

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:[10]

$$\ln \text{rate}(\text{g/cm}^2\text{-sec}) = 10.891 - \frac{68618}{T} \qquad (6)$$

Figure 1 shows a comparison of calculated versus experimental corrosion rates. The calculated data shown in figure 1 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. 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) from the surface.

The model was used to extrapolate to higher pressures as shown in figure 2. 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 liquid is predicted to form on the surface due to the shift in the CVC. Details of the effects of gas flow rate, added hydrocarbon, and the presence of dissociated hydrogen will be discussed in the presentation and full paper.

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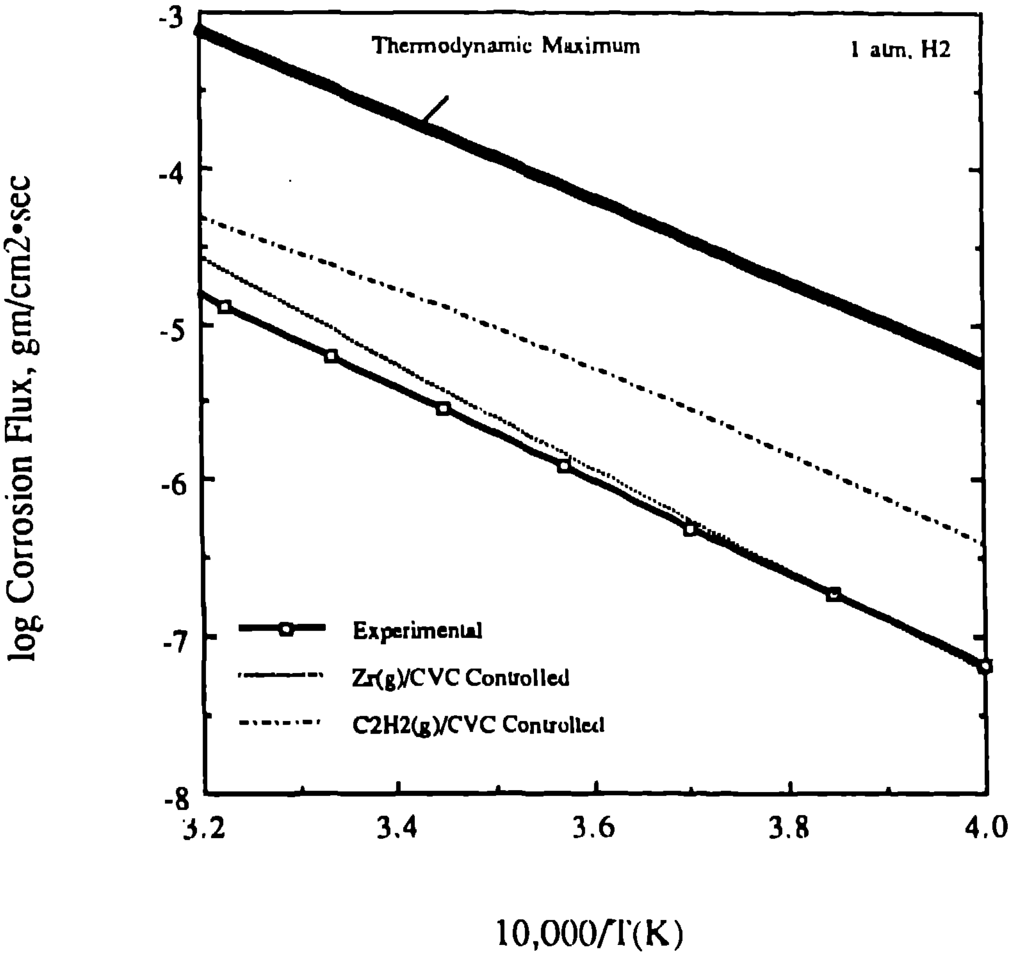

Figure 1. Arrhenius plot of corrosion flux comparing measured and calculated rates.

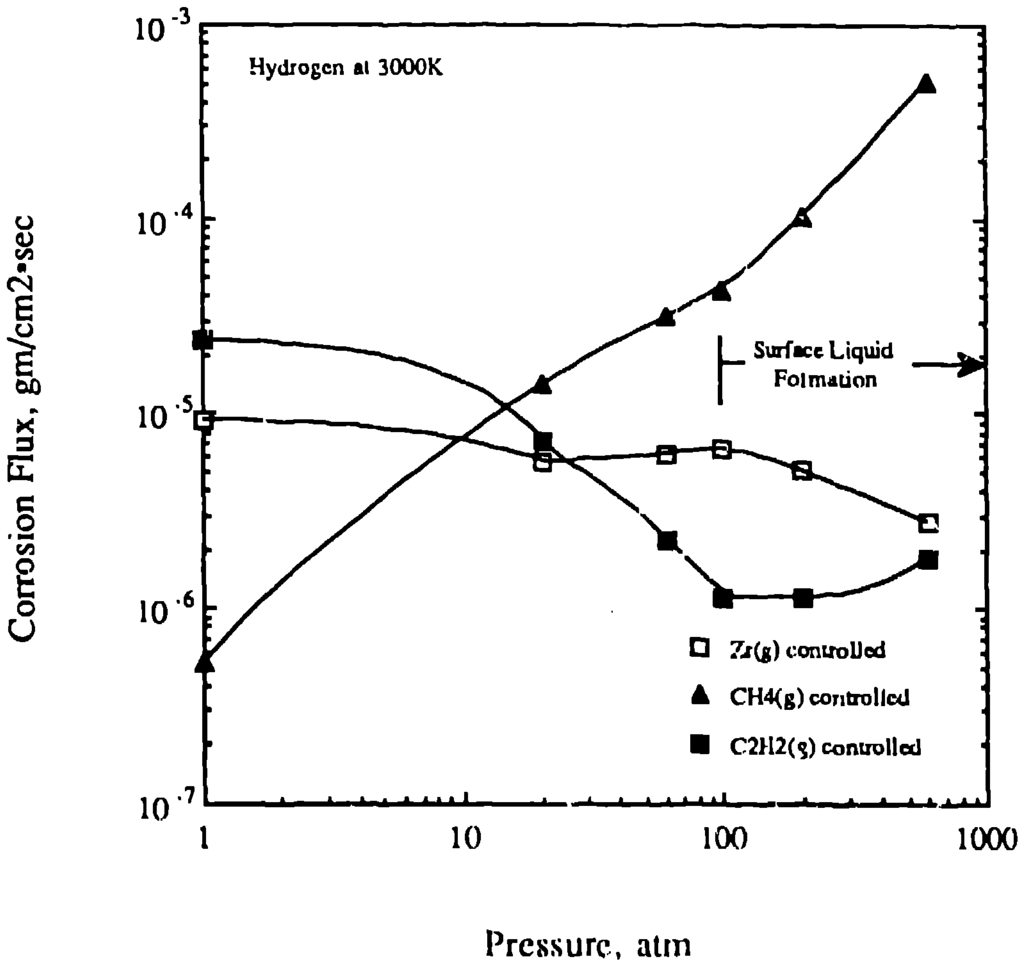

Figure 2. Calculated corrosion flux versus hydrogen pressure under three assumptions: that corrosion is rate limited by the gaseous transport of Zr, CH_4, and C_2H_2.