

Modeling High-Temperature Erosion of Refractory Metals in Hydrogen Bearing Atmospheres

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ABSTRACT. A model for predicting oxidation rates of high melting-point metals in H₂/H₂O atmospheres is developed using thermodynamic equilibrium calculations and mass-transfer principles. From this model the erosion rate of high melting-point metals is calculated under oxidation condition controlled by the step of mass transfer through the boundary layer. This relatively simple model is shown to give reasonable agreement with reported experimental data for the rate of erosion of rhenium. Temperatures in the range from 2000 to 3000 K were used.

KEYWORDS: erosion, refractory metals, high temperature oxidation, high temperature erosion modeling.

1. Introduction

The use of the high melting-point metals, W, Re, and Mo is severely limited by the tendency of these metals to form volatile oxides upon exposure to oxidizing atmospheres at high temperatures. The erosion of these metals when exposed to oxygen at various oxygen pressures and temperatures has been extensively studied ^[1, 2], but very few studies have been carried out in atmospheres containing hydrogen. Evidently, the erosion in hydrogen-water vapor atmospheres has a different character than that in atmospheres containing only oxygen. This paper presents a model for evaluating the erosion rate of refractory metals in hydrogen-water vapor atmospheres. The model relies on principles of thermodynamic equilibrium and convective mass transfer and should be easily

extended to deal with atmospheres containing hydrocarbons. Such atmospheres are generated by combustion of fuels containing hydrocarbons. An application of great technological significance for the use of refractory metals is in spacecraft thruster engines, where this model is potentially useful for prediction of the lifetime of such apparatus.

2. Mechanism of Oxidation

Most of the experimental studies of the oxidation of the refractory metals at high temperatures have been carried out in vacuum chambers at low partial pressures of oxygen ^[1, 3-6]. Thus, the mechanism of oxidation and evaporation that applies in this case is that oxygen molecules strike the surface at a rate determined by the gas partial pressure. Some fraction of the molecules are chemisorbed and react with the metal to form an oxide molecule, which immediately leaves the surface and deposits on the wall of the vacuum chamber. The overall evaporation rate is then determined by the details of the adsorption and oxidation of oxygen on the surface and the various reactions that occur to form different oxide species. The models for these processes can be quite complex since the chemical species that leave the surface may not be the most stable ones predicted by thermodynamic equilibrium considerations. For example the study of oxidation of tungsten by Schissel and Trulson ^[7] found that for tungsten exposed to an oxygen partial pressure of 2.1×10^{-4} torr the composition of the oxide changed with increasing temperature from W_3O_9 at 1400 K to WO at 3000 K. Thermodynamic data ^[8] indicate that WO_3 is the most stable gas phase over this entire temperature range. Thus the results of Schissel and Trulsen work emphasize the fact that the oxidation rate of tungsten under the given conditions is controlled by the complex series of steps taking place on the surface of the metals. This also indicated by the results of Bartlett and McCamont ^[9] showing that the oxidation rate is dependent on the crystallographic orientation of the surface plane. In this paper, the complex oxidation reaction taking place on the surface will be referred to by the term "surface-process".

As the total gas pressure approaches 1 atm the mean free-path of the gas molecules becomes very small compared to the distance separating the hot metal from cooler parts of the apparatus and direct flight of the evaporating gas molecules to the chamber walls is no longer possible. In this case it may happen that some of the evaporating molecules will return to the sample. At atmospheric pressure the mean free-path is so small that we can think in terms of a very narrow region of gas near the metal surface where chemical equilibrium is established between the various gas species and the metal. In this case the reaction rate will be mainly controlled by diffusion of the gaseous species across the boundary layer separating the metal surface from the bulk gas

flow, Figure (1). Actually the two steps of the evaporation process must take place in series so that the overall reaction rate will be given by: ^[10]

$$R_{total}^{-1} = R_{surface-process}^{-1} + R_{mass-transfer}^{-1} \quad (1)$$

However, the surface-process rate is generally much greater than the mass-transfer rate so the total reaction rate is essentially equal to the mass-transfer rate. The model for the mass-transfer rate will be developed in the next section of this paper.

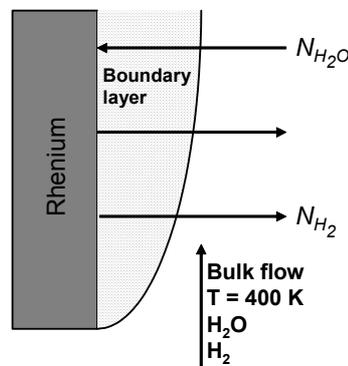
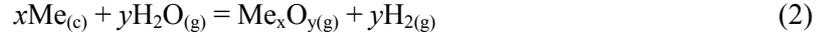


Fig. 1. Schematic sketch for the diffusion process across boundary layer surrounding the rhenium specimen.

3. Erosion Rate Controlled By Diffusion

At relatively high gas pressure the evaporating metal oxide molecules form a boundary layer next to the metal surface. This boundary layer acts as a wall that back-reflects some of the evaporating oxide molecules back to the surface ^[11]. In addition, since the evaporation rate of metal oxides is determined by the amount of the oxidizing molecules at the surface, the presence of this boundary layer reduces the amount of oxidizing molecules arriving to the surface compared to the amount present beyond the boundary layer. Further, when the vapor pressure of the metal is low, the oxidation reactions will be confined to the surface of the metal. Under this condition, we propose the following mechanism for erosion of refractory metals in hydrogen bearing atmospheres. In the boundary layer near the surface, equilibrium is established between Me, H_{2(g)}, H_{2O(g)}, and metal oxides Me_xO_{y(g)} through the stoichiometric equation:



The partial pressure of oxygen is expected to be much lower than that for H_2 or H_2O in the high temperature range considered here. Thus, from Equation (2) for every y moles of water diffusing to the surface x moles of Me are consumed and diffuse from the surface to the bulk to maintain the equilibrium condition at the surface. The Me consumed from the surface will be in an oxide form of an oxidation state that depends on the type of the metal. An equal number of moles of hydrogen to the number of moles of water consumed will be produced and diffuse to the bulk. In the particular case of convective mass flow we can assume approximate equality of the diffusion coefficients ^[12]. In addition, from Fick's law the quantity of diffusing species can be related to the pressure gradient across the boundary layer. Now, if N is equal to the molar flux, then:

$$N_{\text{H}_2} = -N_{\text{H}_2\text{O}} \quad (3)$$

$$N_{\text{H}_2\text{O}} = -\sum_{x,y} yN_{\text{Me}_x\text{O}_y} \quad (4)$$

Since the dimension of the metal specimen is expected to decrease at a very slow rate with time, i.e., the diffusion path will change by small amounts over a long period of time, a quasi-steady-state convective mass transfer model can be used to predict the erosion rate of the metal.

From the mass diffusion equations around the boundary layer we can define the mass transfer driving force for component j (B_j) as:

$$B_j = \frac{x_j^\infty - x_j^o}{x_j^o - x_j^t} \quad (5)$$

where;

x_j^∞ : bulk mass fraction of component j (kg of j /kg of mixture).

x_j^o : equilibrium mass fraction of component j .

x_j^t : transferred substance state mass fraction of component j .

The t state (the transferred substance state) is located at the surface where Me atoms transfer from the metal to the boundary layer. Material transfer across

this state boundary occurs by convection. For the particular case considered here the metal is the only transferred substance then $x_{Me}^t = 1.0$.

For the current process which involves a reaction at the surface, it is more convenient to express the mass fraction in terms of chemical elements rather than compounds. A compound can be destroyed and created in a reaction while the chemical elements are conserved through the reaction. The chemical elements involved here are; Me, O and H. Since H_2 as a molecule that appears in both the reactants and the products (Equation 2), we can use molecular hydrogen (H_2) in the elemental balance equation. Consequently, the mass fractions for these elements at any point can be expressed by:

$$X_i = \sum_j a_{i,j} x_j \quad (6)$$

where;

$a_{i,j}$: mass fraction of element i in component j .

x_j : mass fraction of component j in the total mixture.

X_i : mass fraction of element i in the total mixture.

Since the vapor pressure of the metal is expected to be very low then $x_{Me}^o = 0.0$ will be assumed at the surface. At the bulk, the mass fractions for all components are assumed to be given. Now, from the elemental mass fraction Equations (6) for the three states, the driving force for diffusion for element i (B_i) can be expressed in terms of the mass fractions of the components involved at equilibrium.

Assuming uniform constant property boundary layer, under which; density, viscosity and diffusivity of the boundary layer fluid are thought to be close to constant throughout the boundary, then the Me mass transfer rate (R_{Me}) is defined as: ^[13]

$$R_{Me} = g_{Me} B_{Me} \quad (7)$$

where, g_{Me} is the mass transfer conductance. The complexity arises here from the dependency of g_{Me} on B_{Me} because of dependency of the normal velocity at the wall on R_{Me} . However; for a constant bulk flow and for momentum

transfer normal to the direction of the bulk flow, the following correlation can be used to calculate g_{Me} :^[13]

$$\frac{g_{Me}}{G_{\infty}} = 0.0287 \left(\frac{\mu_{mix}}{\rho_{mix} D} \right)^{-0.4} \text{Re}^{-0.2} F_{Me} \quad (8)$$

where;

g_{Me} : mass transfer conductance, kg/(s.m²)

G_{∞} : net mass flow rate, kg/(s.m²)

μ_{mix} : dynamic viscosity, Pa.s

ρ_{mix} : density, kg/m³

F_{Me} : blowing factor, $\ln(1 + B_{Me}) / B_{Me}$

Re : Reynolds number

D : diffusion coefficient in the boundary layer

The diffusivity in the boundary layer D can be calculated through Hirschfelder equation:^[14]

$$D = \frac{0.001858 T^{3/2} \left[\frac{1}{M_{H_2O}} + \frac{1}{M_{Me_xO_y}} \right]^{1/2}}{P \sigma^2 \Omega_D} \quad (9)$$

where;

T : boundary layer temperature, K

M : molecular weight.

P : absolute pressure, atm.

σ : collision diameter, Angstroms.

Ω_D : collision integral.

D : Diffusivity, cm²/s.

The viscosity can be calculated assuming nonpolar molecules through: [15]

$$\mu_j = \frac{2.6693 \times 10^{-6} \sqrt{M_j T}}{\Omega_D \sigma^2} \quad (10)$$

where M_j is the molecular weight of the j^{th} species. Whereas, the viscosity of the mixture can be calculated from the component viscosities by Wilk's relation:

$$\mu_{mix} = \sum_i^n \frac{\tilde{x}_i \mu_i}{\sum_i \tilde{x}_i \Phi_{ij}} \quad (11)$$

$$\Phi_{ij} = \frac{1}{\sqrt{8}} \left(1 + \frac{M_i}{M_j} \right)^{-1/2} \left[1 + \left(\frac{\mu_i}{\mu_j} \right)^{1/2} \left[\frac{M_j}{M_i} \right]^{1/4} \right]^2 \quad (12)$$

where;

\tilde{x}_i : mole fraction of i^{th} species.

Now, let us go back to the mass fraction equations. The mass fractions for the components H_2 , H_2O and Me_xO_y at the surface are equal to the ratio of density of the given component to the total density of the mixture at the surface;

$$x_j = \frac{\rho_j}{\rho_{mix}} \quad (13)$$

Assuming ideal gas law, the density can be calculated from;

$$\rho_j = P_j \frac{M_j}{RT} \quad (14)$$

where, P_j is the partial pressure at the surface for component j . From our assumption of thermodynamic equilibrium prevailing at the surface, we can relate the partial pressure to the free energy of the reaction by:

$$K_{Me_xO_y} = e^{\frac{-\Delta G_{Me_xO_y}^0}{R_{gas}T}} = P_{Me_xO_y} \left(\frac{P_{H_2}}{P_{H_2O}} \right)^y \quad (15)$$

As mentioned before, under diffusion control the erosion rate will be equal to the mass transfer rate (R_{Me}). Thus, the erosion rate in in/hr is related to the mass transfer rate by:

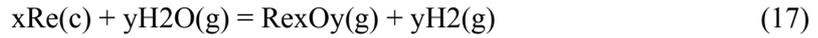
$$\text{Erosion Rate, (in/hr)} = 141.7323 \frac{R_{Me}}{\rho_{Me}} \quad (16)$$

Therefore, by solving Equations (3) through (16), the erosion rate can be calculated.

4. Application Of Diffusion Model To Erosion Of Rhenium

Experimental investigations on the oxidation of Re in oxidizing atmospheres at high temperatures showed that the surface of the Re after exposure to the oxidizing atmospheres, to have a highly reflective surface as though electropolished ^[16]. Other studies reported this behavior even after removal of more than 0.02" from the diameter. This indicates that the oxides formed at high temperature have a large volatility that evaporate as soon as it is formed and the oxide layer does not form.

In the case of Re it was found the oxides that can form upon oxidation include ReO₂, ReO₃ and Re₂O₇ ^[4,17,18]. Other oxides states are also possible but they are unstable and there is less known about them. Among these different oxides Re₂O₇ was believed to be the predominant oxide upon oxidation of Re ^[4,16,19]. Re₂O₇ is a volatile oxide that melts at 296°C and boils at 362°C under 1 atm pressure ^[16]. Studies on rhenium interaction with water vapor using the thermal desorption mass spectrometry methods confirmed the dissociation of the H₂O_{ad} molecules and evolution of H₂ which started at T > 200 K ^[20]. Accordingly, the stoichiometric reaction equation for the formation of Re oxides is:



The elements involved here are; Re, O and H. Thus from Equations (6), the mass fraction for these elements can be expressed by:

$$X_{\text{Re}} = 0.769x_{\text{Re}_2\text{O}_7} + 0.795x_{\text{ReO}_3} + 0.853x_{\text{ReO}_2} + x_{\text{Re}} \quad (18)$$

$$X_{\text{O}} = 0.231x_{\text{Re}_2\text{O}_7} + 0.205x_{\text{ReO}_3} + 0.147x_{\text{ReO}_2} + 0.889x_{\text{H}_2\text{O}} \quad (19)$$

$$X_{\text{H}_2} = x_{\text{H}_2} + 0.111x_{\text{H}_2\text{O}} \quad (20)$$

For the purpose of solving the diffusion model mentioned before for this system; Re/H₂-H₂O vapor mixture, the free energies for Re₂O₇, ReO₃ and ReO₂

required in Equations (15) were taken from the limited reported data in the literature^[18]. The collision diameter and the collision integral in Equation (9) were calculated for water only since these data for Re_xO_y are not available^[14]. The boundary layer temperature was taken as the arithmetic average between the bulk and the specimen temperatures.

For the other variables, values usually utilized in typical experiments were used. For this Re sample was assumed in form of a cylinder (1 inch long and 0.75 inch in diameter) that was inductively heated to different high temperatures in the range 1800 to 3000 K. The heated specimen was assumed to be exposed to mixtures of $\text{H}_2\text{-H}_2\text{O}$ vapor of different ratios at temperature of $T = 400$ K. $P_{\text{H}_2\text{O}} / P_{\text{H}_2} = 1, 2.33$ and 10129 were used. This range for the $\text{H}_2\text{O}/\text{H}_2$ ratios covers the range of high hydrogen content to almost no hydrogen in the mixture. The case of almost no hydrogen content is of interest in order to compare the model prediction with the only available date reported by Kilpatrick *et al.*^[16] Evidently, at the other $\text{H}_2\text{-H}_2\text{O}$ mixture ratios, available experimental data are lacking in the literature. One possible reason is the difficulty to simulate these conditions in a laboratory setting.

An atmospheric total pressure (101.3 kPa) was assumed. Two flow rates of 1.5 l/min and 19 l/min were used. For the case when $P_{\text{H}_2\text{O}} / P_{\text{H}_2} = 1$, the bulk mass fractions for the elements involved are:

$$X_{\text{Re}}^{\infty} \approx 0.0 \quad (21)$$

$$X_{\text{O}}^{\infty} = 0.8 \quad (22)$$

$$X_{\text{H}_2}^{\infty} = 0.2 \quad (23)$$

Similarly the fractions for the elements can be calculated at the other two pressure ratios.

A computer algorithm was utilized to solve the equations involved in the model. The model solutions under these conditions are shown in Fig. 2. This figure includes some experimental results reported in the literature at different conditions. Of these results Kilpatrick *et al.*'s data^[16] was reported at similar conditions used in the model, with which the model's predictions are in good agreement.

As of the effect of hydrogen pressure on the erosion process, the model shows a very large reduction in the erosion rate as the hydrogen pressure increased. This finding, as shown in Fig. 2, is more pronounced at lower

temperatures. Further, when the data for erosion of Re at $P_{H_2O}/P_{H_2} = 1$ was fitted to Arrhenius relationship the activation energy was 134 kcal/mol.

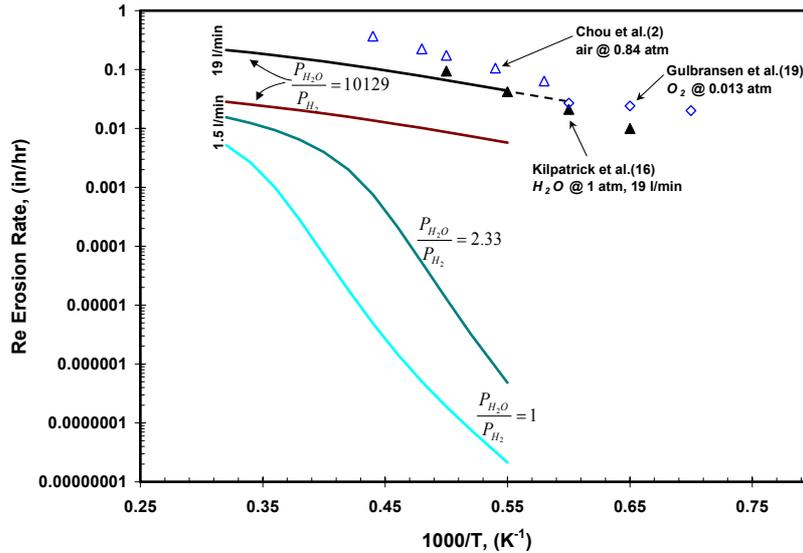


Fig. 2. Solutions to the erosion model for rhenium/(H₂O-H₂) system at different P_{H_2O}/P_{H_2} ratios as a function of temperature. Included in the figure some reported experimental data at various experimental conditions.

5. Discussion

The model proposed here can be used to calculate the erosion rate of refractory metals when the total pressure is relatively high. This model which is lacking in the literature can be used to simulate the erosion phenomena under both current and expected future conditions for applications of these materials. On the other hand, when the pressure is very low, the mean free-path of the gas molecules becomes larger than the diameter of the vessel. In this case the surface-process can control the overall reaction rate. For this case when the pressure is very low, the model proposed by Sheman *et al.* [4] that is based on adsorption and desorption kinetics at the surface can be used to calculate the erosion rate. It is worthwhile to note that by combining Sheman's model along with our model through Equation (1), the erosion rate can be calculated at any chamber pressure.

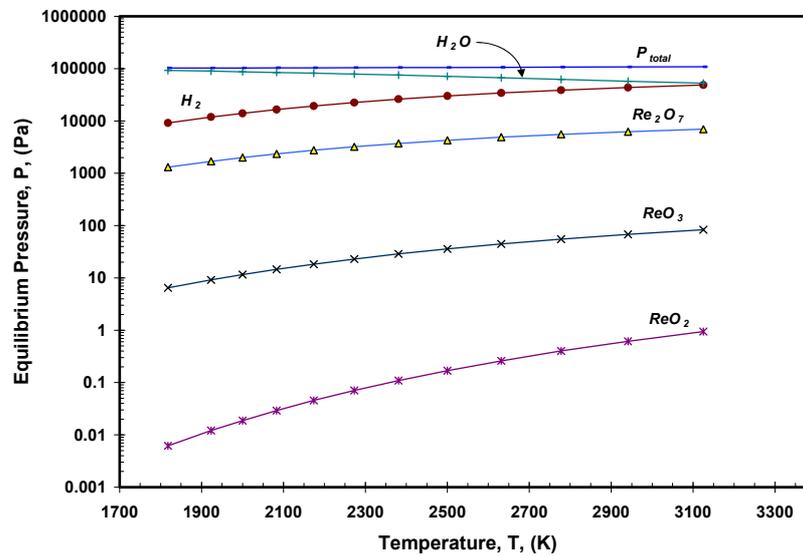


Fig. 3. Calculated equilibrium partial pressures for rhenium oxides at different temperature.

Application of the model to the particular case of Re system considered in this study was seen to give good agreement with experimental data. For this particular system studied, the equilibrium partial pressures of the involved gases at the surface as predicted from the model are shown in Fig. 3. It is clear that Re_2O_7 contributes more than the other oxides to the erosion rate of Re, in agreements with most of the studies reported in the literature. However, Sheman *et al.* [4] proposed ReO_4 as a stable oxide. Nevertheless, in their study they doubted the stability of this oxide and the validity of the thermodynamic data reported by Glassner [8]. Furthermore, when we included this oxide in our model using Glassner's data, the model predicted a much higher erosion rate than the experimental rates.

For engineering design where it is of interest to know the maximum erosion rate that can occur, it is possible to calculate the maximum rate in light of the current formulation. Maximum erosion rate can occur when the reaction rate at the surface is very fast i.e. all water arriving to the surface is reacting thereby the concentration of water at the surface will be zero. For the case of Re system discussed in this study, assuming the predominant oxide Re_2O_7 is the only oxide forming. Then, the mixture at the surface will contain only H_2 and Re_2O_7 . Thus Equations (18) and (19) will reduce to:

$$X_{\text{Re}} = 0.769x_{\text{Re}_2\text{O}_7} + x_{\text{Re}} \quad (24)$$

$$X_{\text{O}} = 0.231x_{\text{Re}_2\text{O}_7} + 0.889x_{\text{H}_2\text{O}} \quad (25)$$

To calculate the erosion rate of Re by the model mentioned, the concentration of Re_2O_7 at the surface is needed. However, from the fact that any linear combination of a conserved property is again a conserved property^[13], then it is possible to construct a linear combination of these two equations in a way that the concentration of Re_2O_7 does not appear in the resulting equation i.e.:

$$X' = X_{\text{Re}} - \frac{0.769}{0.231}X_{\text{O}} \quad (26)$$

Consequently, by evaluating the parameter X' at the three states; 0, ∞ and t , the driving force (B) can be calculated. For example when $P_{\text{H}_2\text{O}}/P_{\text{H}_2} = 1$, B will be equal to 2.663. The mass transfer conductance (g) can be calculated from Equation (8). By performing these calculations, the maximum value for g over the temperature range considered here is found to be 0.003 kg/s.m^2 . Therefore, the maximum erosion rate by using Equation (16) is 0.055 in/hr which lie above the maximum rate shown in Figure (2) at this $\text{H}_2\text{O-H}_2$ pressure ratio.

In applying the proposed model in this study, care must be taken to the experimental conditions. For example, when the Re specimen is heated by a direct resistance technique, the reacting gas will be at a lower temperature than that on the specimen's surface and the molecules will not be dissociated. However, if the specimen is heated by thermogravimetric technique where the specimen is suspended in a furnace, the gas will have nearly the same temperature as the specimen. In this case depending on the temperature and the pressure, the dissociation of the water will be more pronounced and has to be considered in the model^[21].

6. Summary

The erosion mechanism of refractory metals in $\text{H}_2/\text{H}_2\text{O}$ atmospheres was studied. Depending on the temperature and the pressure there can be two possible mechanisms. At pressures much lower than atmospheric pressure, surface-processes based mechanism controls the rate, while at higher pressure diffusion through the boundary layer near the surface was found to control the

over-all erosion rate. A model for the erosion rate under diffusion control was developed on the basis of quasi-equilibrium treatment through a convective mass transfer theory. Application of the model to the particular case of Re system was seen to give good agreement with experimental data. Further, through the proposed model it was able to predict the erosion rate at conditions that can be encountered in real life situations but very difficult to simulate in laboratory settings. Therefore, The model aids in understanding the erosion of refractory metals and explains the effects of the gas pressure on the erosion phenomena.

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