VOLATILIZATION FROM PCA STEEL ALLOY

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AUG 22 1996

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ABSTRACT

The mobilizations of key components from Primary Candidate Alloy (PCA) steel alloy have been measured with laboratory-scale experiments. The experiments indicate most of the mobilization from PCA steel is due to oxide formation and spalling but that the spalled particles are large enough to settle rapidly. Based on the experiments, models for the volatilization of iron, manganese, and cobalt from PCA steel in steam and molybdenum from PCA steel in air have been derived.

I. INTRODUCTION AND BACKGROUND

The potential for mobilization and transport of activation products in fusion reactor materials is an important safety consideration for fusion reactor safety. To address concerns about mobilization, a program to provide information from several materials that may be used in fusion reactors has been carried out over the last several years at the Idaho National Engineering Laboratory. This paper describes the data and models developed from measurements with PCA steel in steam and air environments.

The models described in this paper are based primarily on measurements made in the VAPOR (Volatilization of Activation Products Reactor) apparatus. Figure 1 is a schematic of the apparatus used for most experiments. In this apparatus, alloy samples 25 mm in diameter and 4 mm thick were heated with either an induction coil (as shown in the figure) or a tube furnace. Either air or steam flowed past the specimen at 5 liters (air) or 2.5 liters (steam) per minute. The quartz tube

Figure 1. Schematic of the VAPOR apparatus for measuring mobility of elements from materials.

containing the specimen was 3.8 cm in diameter. Another quartz tube located downstream from the sample tube and containing a quartz wool filter trapped mobilized condensates. Residual gas from steam experiments was collected in a volumetric cylinder and used with sample weight gains to determine the amounts of hydrogen generated by steam reactions.

II. GENERAL BASIS FOR MODELS

In the most straightforward cases, volatilization occurs from the surface of a pure species into a

vapor of the same species. In this case, the flux of volatilizing material is proportional to the difference between the vapor concentration (or, with use of an equation of state like the ideal gas law, the vapor pressure), the vapor equilibrium concentration (or pressure), and a mass transfer coefficient that is a function of the vapor flow, surface geometry, and certain gas properties:

$$J = k_w [C_{eq} - C_{bulk}] = \frac{k_w M}{R T} [P_{eq} - P] \quad (1)$$

where

J = mass flux of evaporating chemical species (kg/m²-s)

k_w = mass transfer coefficient (m/s)

C_{bulk} = average (bulk average or cup-mixing average) concentration of vapor species (kg/m³)

C_{eq} = equilibrium concentration of vapor species (kg/m³)

M = molecular mass of the volatilizing species (kg/kg-mole)

P = bulk average pressure of vapor species (Pa)

P_{eq} = equilibrium pressure of vapor species at surface (Pa)

R = ideal gas law constant, 8314 kg m²/(s²-kg-mole-K)

T = temperature of the oxide surface (K).

The bulk average concentration and pressure of the vapor species in the gas is usually small so that

$$J \approx k_w C_{eq} = \frac{k_w M}{R T} P_{eq} \quad (2)$$

There are a number of effects that have the potential to complicate volatilization calculations. For instance, if the surface is not a pure species, the equilibrium pressure (concentration) of the volatilizing species in Equation (1) or (2) is replaced by the mole fraction of the volatilizing species at the surface of the condensed phase times an activity coefficient that is characteristic of the surface material and the volatilizing species. Other complications include surface reactions and concentration gradients in the alloy.

A. Effect of Surface Reactions

Reactions with the gas phase may alter volatilization by reacting with the surface layer to form a more or less volatile species. If a less volatile reaction layer like an oxide of some metals is formed on the surface, this oxide may impede the transport of volatile material alloyed with the metal under the oxide and it may mobilize material by spalling at some point. On the other hand, alloys in a steam environment often react with the steam to form an oxide and then a volatile hydroxide. In cases where gas phase reactions affect volatility, the equilibrium concentration or pressure must be calculated from the equilibrium constant and the concentrations of the reactants and any other products of the reaction.

For example, if a species, A, reacts with a species, B, to yield products, C and D, according to the equation

the thermodynamic equilibrium constant is the ratio of the activities of the products divided by the reactants, all raised to the power of the number of molecules of each species in the equation¹,

$$K_{xy} = \frac{[xy]_C^c [xy]_D^d}{[xy]_A^a [xy]_B^b} \quad (4)$$

Assuming ideal solution behavior yields an expression for the equilibrium constant in terms of the gas pressures and the mole fractions of reacting solid alloy components. For example if species B, C, and D are gases but A is a solid component present at a mole fraction x_A then,

$$K_P = \frac{P_C^c P_D^d}{x_A P_B^b} P^{[b-c-d]} \quad (5)$$

where

P = total pressure of system (Pa)

P_B = equilibrium pressure of vapor species B (Pa).

The thermodynamic equilibrium constant can be calculated from the change in the Gibbs function

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during the reaction,

$$K_{xy} = \exp \frac{-\Delta G_{\text{reaction}}^{\circ}}{RT} \quad (6)$$

Two corollaries of this result will be encountered. If there is only one reaction product, Equation (5) with $d = 0$ is appropriate. If the reaction is really a congruent evaporation with only one species on each side of Equation (3), Equation (5) with $b = d = 0$ is appropriate.

B. Effect of Concentration Gradients in the Alloy

Often, the mole fraction of the volatilizing species at the surface is equal to the mole fraction of the species in the bulk sample. However, if one component of an alloy volatilizes at a rate significantly different than another would at the same concentration, the volatilization may be controlled by the rate of diffusion of the volatile component through the volume of the condensed material to the surface.

Figure 2 is a schematic showing the path taken by minority alloy components that volatilize more rapidly than major alloy components. Minority component mass in the interior of the alloy must diffuse to the surface where it may interact with the gas environment of the alloy. Transport from the surface is driven by the concentration gradient of the component in the gas. Solution of Fick's second law for a slab in the gas shows the flux through the surface is

$$J(t) = \frac{2 D_{i, \text{Alloy}}}{b} [C_0 - C_{\text{surf}}(t)] \sum_{n=0}^{\infty} \exp \frac{-[n + \frac{1}{2}]^2 \pi^2 \frac{D_{i, \text{Alloy}} t}{b^2}} \quad (7)$$

where

- C_{surf} = surface concentration (kg/m^3)
- C_0 = initial minority component concentration (kg/m^3)
- $D_{i, \text{Alloy}}$ = diffusivity of minority species in the alloy (m^2/s)
- t = time (s)
- b = slab thickness (m).

An expression for the volatilization rate that considers both transport to the surface from inside the alloy and subsequent evaporation from the alloy surface can be obtained by assuming a steady state, i.e. that the rate at which the element is supplied to

Figure 2. Schematic of diffusion of alloy components from the interior of the alloy to the surface, evaporation or possible reactions with the gas at the surface, and diffusion into the bulk gas.

the surface is equal to the rate at which volatilization carries the element away from the surface. This assumption along with Equation (2), Raoult's law, and Equation (7) yields the expression,

$$J(t) = \frac{2 D_{i, \text{Alloy}}}{b} [C_0 - C_{\text{surf}}(t)] \sum_{n=0}^{\infty} \exp \frac{-[n + \frac{1}{2}]^2 \pi^2 \frac{D_{i, \text{Alloy}} t}{b^2}} \quad (8)$$

$$= k_w C_{\text{eq}} = k_w x \gamma C_{\text{eq}}(\text{pure species})$$

Both C_{surf} and C_{eq} are proportional to the surface mole fraction of the minority component so this equation can be solved to find the quasi steady state surface mole fraction, $x(t)$. The mole fraction can then be used to find the flux from either side of Equation (8).

The surface concentration is related to the surface mole fraction by the density of the solid and molar masses of the components,

$$C_{\text{surf}} = x \rho_{\text{Alloy}} \frac{M}{M_{\text{Alloy}}} \quad (9)$$

where

- ρ_{Alloy} = density of the alloy (kg/m^3)
- M_{Alloy} = kg-molar mass of the alloy (kg/kg-mole).

The equilibrium concentration is related to the equilibrium vapor pressure by the ideal gas law,

$$C_{eq} = \frac{M}{RT} P_{eq} \quad (10)$$

and the equilibrium vapor pressure is related to the surface mole fraction by an equation that depends on the surface reaction.

For the PCA alloy, concentration gradients are significant for the volatilization of molybdenum oxide in air but not for the volatilization in steam. In the case of molybdenum, the volatilization is a congruent evaporation so

$$P_{eq} = x P_{standard} \exp \frac{-\Delta G_{condensed \rightarrow vapor}^T}{RT} \quad (11)$$

where

$P_{standard}$ = the standard state pressure (usually one atmosphere)

For congruent evaporation, solution of Equations (11), (10), (9), and (8) for $x(t)$, and substitution of the resultant expression for $x(t)$ back into Equation (8) yields the following expression for volatilization :

$$J = \frac{C_{1con} x(0)}{1 + \frac{C_{1con}}{C_2(t)}} \quad (12)$$

where

$$C_{1con} = \frac{k_w M}{RT} P_{standard} \exp \frac{-\Delta G_{condensed \rightarrow vapor}}{RT} \quad (13)$$

and

$$C_2(t) = \frac{2 D_{Alloy} P_{Alloy} M}{b M_{Alloy}} \sum_{n=0}^{\infty} \exp \left[-\left(n + \frac{1}{2}\right)^2 \pi^2 \frac{D_{Alloy} t}{b^2} \right] \quad (14)$$

and the activity coefficient, γ , has been assumed to be one.

III. EXPRESSIONS FOR VOLATILIZATION

The composition of austenitic PCA (Primary Candidate Alloy) is similar to 316 stainless steel but differs from 316 stainless steel because of the addition of a small amount of Ti, a slightly lower Cr content, and a slightly higher Ni content. Sixty four mole percent of the alloy is iron, 1.6 mole percent is manganese, 1.1 mole percent is molybdenum and only 0.04 mole percent is cobalt.

A. In Steam

In steam, most of the mass volatilized is iron. However, manganese and cobalt volatilization is more important in some instances because these elements are associated with more active isotopes than the iron. Iron is primarily important as a source of small, easily transported aerosol particles formed from the vapor phase. These particles have the potential to affect the transport of other chemical species by acting as a condensation site for vapor that would otherwise condense on walls. In addition to iron, we have also considered the volatilization of manganese and cobalt in steam because these elements include isotopes with considerable activity.

PCA steel reacts with steam to form hydrogen and an oxide layer. The rate of this reaction is given by Leistikow's correlation for the net oxygen uptake²

$$J_o = \frac{1}{2} \left[10^{-6} \frac{kg}{mg} \right] \left[10^2 \frac{dm^2}{m^2} \right] \sqrt{2.8 \times 10^{11} \exp \left(-\frac{227,000}{8.29 T} \right)} t^{-\frac{1}{2}} \left[\frac{mg O}{dm^2 s} \right] \quad (15)$$

where

T = temperature (K)

J_o = oxygen mass flux to metal surface (kg/m²-s)

The data to be discussed below are reasonably consistent with the assumption that there is a quasi-equilibrium at the oxide surface described by the equation

where M is Fe, Mn, or Co.

In this case, Equations (3) and (5) without the second reaction product, together with Equation (6) show

$$P_{eq} = x P_{H_2O} \exp \frac{-\Delta G_{reaction}^T}{RT} \quad (17)$$

Equation (2) rather than Equation (12) is appropriate for use with Equation (17) because the main components of the oxide all volatilize at approximately the same rate, thus avoiding concentration gradients in the oxide layer.

1. Iron Volatilization

Combining Equations (2) and (17) for this case yields

$$J_{Fe(OH)_2} = \frac{k_w M}{R T} \times P_{H_2O} \exp \left(-\frac{\Delta G_{reaction}^\circ}{R T} \right) \quad (18)$$

The change in the Gibbs function needed to calculate the iron hydroxide mass flux with Equation (18) was obtained by adding and subtracting the Gibbs function changes for several reactions given by Belton and Richardson³ or Kubaschewski and Alcock⁴ to obtain the Gibbs function change corresponding to Equation (16) with $M = Fe$. Thus Equation (18) becomes

$$J_{Fe(OH)_2} = \frac{k_w 1.08 \times 10^{-2}}{T} \times P_{H_2O} \exp \left(-\left(\frac{23,721}{T} - 4.95 \right) \right) \quad (19)$$

2. Cobalt Volatilization

The change in the Gibbs function needed to calculate the cobalt hydroxide mass flux with an equation similar to Equation (18) was obtained by adding and subtracting the Gibbs function changes for several reactions given by Belton and Jordan⁵ and by Kubaschewski and Alcock⁴ to obtain the Gibbs function change corresponding to Equation (16) with $M = Co$. In this case,

$$J_{Co(OH)_2} = \frac{k_w 1.12 \times 10^{-2}}{T} \times P_{H_2O} \exp \left(-\left(\frac{27,795}{T} - 6.64 \right) \right) \quad (20)$$

3. Manganese Volatilization

To model the volatilization of manganese we assumed the chemistry of the volatilization of this element is similar to the volatilization of iron, which is next to manganese in the periodic table of the elements. The main difference between the volatility of the manganese and the volatility of iron or cobalt from PCA steel should be the mole fraction of the iron, manganese or cobalt component of the alloy and not the chemical differences of the elements.

The validity of the modeling for iron, cobalt, and manganese was tested by calculating the volatilization of manganese from PCA steel and comparing the calculation results to data from VAPOR experiments. Figure 3 shows the calculations and data are consistent.

Figure 3. Calculated and measured volatility fluxes for iron, manganese and cobalt.

B. In Air

In air, most of the mass volatilized is molybdenum. Like iron in steam, this element is not important because of its own activity but rather because it may affect the transport of other species.

The volatility of molybdenum in air is controlled by the vapor pressure of the oxide MoO_3 but the alloy matrix does not volatilize significantly. In this case, Equation (12) is the appropriate expression for calculating volatilization flux. An expression for the equilibrium vapor pressure required to use Equation (12) was obtained from Kubaschewski and Alcock's textbook⁴

$$P_{eq} = x \exp \left[-\frac{1248}{T} + 26.7249 - 4.02 \log_{10}(T) \right] \quad (21)$$

where

P_{eq} = equilibrium vapor pressure of the MO_3 oxide over the surface (Pa).

The diffusivity of molybdenum in PCA steel needed to calculate the factor C_2 of Equation (14) was obtained from Smithells⁶ which recommends a value of 2.3 to $3 \times 10^{-13} \text{ m}^2/\text{s}$ at 1200°C .

The calculated mass flux of molybdenum oxide from a 1 mm thick sample versus reciprocal temperature after 1, 5 and 20 hours in a typical

laminar flow (Reynolds number 22) at 1473 K was 1.70, 1.09, and 0.66 g/m²-hr, respectively. This flux is approximately the same as the flux of iron from PCA steel in steam for the first several hours but the molybdenum flux decreases with time as the molybdenum is depleted from the sample and the concentration gradient becomes too small to drive diffusion through the non-volatile components.

IV. CONCLUSIONS

Although most of the mass mobilized from PCA steel is spalled oxide layer, this mass is in the form of large particles that settle rapidly. In air, there are also small particles of condensed molybdenum trioxide vapor but these particles are not a major activation product. In steam, the volatilization of iron, cobalt, and manganese as hydroxide is an important consideration because the cobalt and manganese are significant activation products and all of the hydroxides have the potential to condense as small particles that transport easily. Volatilization models based on oxidation rate equations and equilibrium oxide - hydroxide chemistry are consistent with measured volatilization rates in steam.

ACKNOWLEDGEMENTS

This work was supported by the U.S. Department of Energy, Director of Energy Research, Office of Fusion Energy Sciences, under DOE Contract No. DE-AC07-94ID13223.

This report is an account of work assigned to the U.S. Home Team under Task Agreement No. S 71 TT 44 within the Agreement among the European Atomic Energy Community, the Government of Japan, the Government of the Russian federation, and the Government of the United States of America on Cooperation in the Engineering Design activities for the International Thermonuclear Experimental Reactor ("ITER EDA Agreement") under the auspices of the International Atomic Agency (IAEA). The report has not been reviewed by the ITER Publications Office.

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