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OXYGEN REDISTRIBUTION IN $(U,Pu)O_{2-x}$

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Oxygen redistribution in moderately hyperstoichiometric actinide oxide fuels is satisfactorily described by the mechanism proposed by Rand and Markin[1]. In this model, oxygen is transported solely via gas phase diffusion of H_2O or CO_2, which are assumed to be the principal oxygen-containing species in the gas.[2] In hypostoichiometric mixed oxides, however, the equilibrium pressures of H_2O or CO_2 are so small that other mechanisms of oxygen transport may become significant. In irradiated fuels, gaseous oxides of the fission products cesium and molybdenum are probably important oxygen carriers. At high fuel temperatures, oxygen may be transported by gaseous actinide oxides. For low fuel temperatures ($<\sim 2000°C$) in the absence of fission products, Aitken[3] has suggested that the steady state profile of the O/M ratio in the solid is established by flow of H_2O or CO_2 in the gas phase balanced by solid state diffusion of oxygen in the opposite direction. The influence of the latter process upon oxygen redistribution depends on the diffusion coefficients, densities and flow areas of the solid and gaseous phases. The purpose of this note is to show analytically how these factors affect oxygen redistribution in a closed axial thermal gradient geometry.

Figure 1 shows a piece of fuel which supports a linear temperature gradient in the z-direction and which contains cracks in

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the same direction. The geometry of the fissured solid has been idealized by assigning an average width b to the cracks and specifying their density by associating a thickness 2H of solid with each crack. The system is infinite in extent in the direction perpendicular to the plane of the drawing. The fluxes of the species $ZO=CO_2$ or H_2O and $Z=CO$ or H_2 in the gas in the crack are given by N^g_{ZO} and N^g_Z, respectively. Assuming transport by molecular diffusion, they are given by Fick's law as:

$$N^g_i = -\frac{D^g_i}{RT}\left(\frac{dp_i}{dz}\right), \quad i = Z, ZO \tag{1}$$

where D^g_i is the diffusion coefficient of species i in the gas phase, R is the gas constant and p_i is the partial pressure of species i.

The flux of oxygen in the solid, N^s_O is given by:

$$N^s_O = -D^s_O\left(\frac{dC_O}{dz}\right) = \frac{D_O\rho_s}{270}\left(\frac{dx}{dz}\right) \tag{2}$$

where $D^s_O = A\exp(-E_D/RT)$ is the solid state diffusion coefficient of oxygen, C_O is the concentration of oxygen in the solid, ρ_s is the mass density of the fuel and x is the departure of the O/M ratio from 2.00. The second equality in Eq (2) follows from the relation: $C_O = (2-x)\rho_s/270$.

Since the ends of the system are assumed closed, the condition of dynamic balance requires that the net flux of Z and O across any plane perpendicular to the temperature gradient be equal to zero. For component Z, this condition leads to:

$$N^g_Z + N^g_{ZO} = 0 \tag{3}$$

Using Eq (1) and assuming $D^g_{ZO} \approx D^g_Z$, Eq (3) yields:

$$p_{ZO} + p_Z = \text{constant} \quad . \tag{4}$$

The ratio p_{ZO}/p_Z is controlled by the equilibrium:

$$Z + \frac{1}{2}O_2 = ZO \tag{5}$$

for which:

$$RT\ln(p_{ZO}/p_Z) = \frac{1}{2}\overline{\Delta G}_{O_2} - \Delta G^\circ_{ZO/Z} \tag{6}$$

where $\Delta G^\circ_{ZO/Z}$ is the standard state free energy change of reaction (5) and $\overline{\Delta G}_{O_2} = RT\ln p_{O_2}$ is the oxygen potential of the fuel (equilibrium between the gas and solid at each point has been assumed). Because the oxygen potentials of hypostoichiometric mixed oxides are large and negative, $p_{ZO}/p_Z \ll 1$, and Eq. (4) becomes:

$$p_Z \approx \text{constant} \tag{7}$$

The condition of zero net flux of oxygen across plane A-A in Figure 1 gives:

$$bN^g_{ZO} + 2HN^s_O = 0 \tag{8}$$

Use of Eqs (1) and (2) in Eq (8) yields:

$$Ge^{-E_D/RT}\frac{dx}{d(z/L)} = \frac{d(p_{ZO}/p_Z)}{d(z/L)} \tag{9}$$

where E_D is the activation energy of solid state diffusion of oxygen and G is:

$$G = \left(\frac{A}{D^g_{ZO}}\right)\left(\frac{\rho_s/270}{p_Z/RT}\right)\left(\frac{2H}{b}\right) \tag{10}$$

A is the pre-exponential factor of the solid state diffusion coefficient. The gas phase diffusion coefficient D^g_{ZO} varies as T^n where $1.5<n<2$. To first approximation, the ratio D^g_{ZO}/T in Eq (10) is constant and may be evaluated at the average temperature. Thus G is a constant which describes the relative importance of oxygen migration in the gas and solid phases. The term A/D^g_{ZO} is a measure of the relative ease of oxygen diffusion in the two phases. The second term is the ratio of the concentrations of the "solvent" through which oxygen migration occurs in the gas and solid phases. The last factor in Eq (10) is the ratio of the flow areas in the two phases. If G=0, Eq (9) yields p_{ZO}/p_Z = constant, which is the Rand-Markin model.

In the general case where G is not zero, Eq (9) may be integrated with the aid of Eq (6). The fuel oxygen potential may be written as $\overline{\Delta G}_{O_2} = \Delta\overline{H}_{O_2} - T\Delta\overline{S}_{O_2}$, and since actinide redistribution has been neglected, the partial molar enthalpy and entropy are functions of x only. Substitution of Eq (6) into Eq (9) yields:

$$\frac{dx}{d(z/L)} = \frac{\left[\dfrac{\frac{1}{2}\Delta\overline{H}_{O_2} - \Delta H^\circ_{ZO/Z}}{RT}\right] \cdot \left(\dfrac{T_o - T_L}{T}\right)}{G\exp\left[-\dfrac{E_D + \frac{1}{2}\Delta\overline{H}_{O_2} - \Delta H^\circ_{ZO/Z}}{RT} + \dfrac{\frac{1}{2}\Delta\overline{S}_{O_2} - \Delta S^\circ_{ZO/Z}}{R}\right]}$$

$$- \frac{1}{2}\left[\frac{1}{RT}\frac{d\Delta\overline{H}_{O_2}}{dx} - \frac{1}{R}\frac{d\Delta\overline{S}_{O_2}}{dx}\right] \qquad (11)$$

Eq (11) may be integrated numerically for a linear temperature variation between T_o and T_L and $\Delta\overline{H}_{O_2}$ and $\Delta\overline{S}_{O_2}$ known as functions

of x from the data presented in Reference 1. The constant of integration is determined by the requirement that the average value of x equal that of the fresh fuel, or:

$$\bar{x} = \int_0^1 x\,d(z/L) \tag{12}$$

Calculations have been performed for T_o = 2000°K, T_L = 1000°K, ρ_s = 11 gms/cm^3, and A = 1.15 cm^2/sec, E_D = 56.7 kcal/mole. These diffusion coefficient parameters pertain to stoichiometric UO_2 [4] and have been used here because no data on oxygen diffusion in hypostoichiometric mixed oxides are available. Since oxygen diffusion in the solid very likely proceeds by a vacancy mechanism on the anion sublattice, use of D_O^S for $UO_{2.00}$ probably underestimates the influence of solid state diffusion. The concentration of anion vacancies in the non-stoichiometric oxide is 2x while in the stoichiometric material the vacancy concentration is equal to the thermal equilibrium value.

For H_2O/H_2 mixtures, the gas diffusion coefficient in Eq (10) has been estimated to be 20 cm^2/sec in 1 atm H_2 at 1500°K. The pressure of H_2 and the temperature in Eq (10) were taken to be 1 atm and 1500°K, respectively. Figure 2 shows the O/M and p_{H_2O}/p_{H_2} profiles for fuel with an average O/M of 1.96 at various values of the crack-to-solid flow area ratio. The curve labelled (b/2H) = ∞ represents negligible transport in the solid; the p_{H_2O}/p_{H_2} ratio is constant along the temperature gradient and the O/M profile is that given by the original model of Rand and Markin. As the crack width becomes smaller, the extent of oxygen redistribution is

decreased and p_{H_2O}/p_{H_2} is no longer constant. For very fine cracks ($b/2H \approx 10^{-5}$) back diffusion in the solid essentially eliminates oxygen gradients in the hot portion of the fuel. Some redistribution occurs near the cold boundary where the oxygen diffusion coefficient in the solid is too low to affect gas phase migration. When there are no cracks ($b/2H \rightarrow 0$), oxygen redistribution cannot take place because there is no mechanism (in the present model) by which oxygen can migrate in the direction which satisfies the thermodynamic tendencies of the system. Solid state diffusion acts to reduce oxygen gradients established by other processes (which may be gas phase transport by any oxygen-bearing species or true thermal diffusion in the solid phase) but cannot by itself cause oxygen redistribution. Molecular diffusion in the solid performs an "enrichment-limiting" function similar to that of back diffusion in isotope separation by the gas centrifuge or thermal diffusion.

The results of the present calculations are in agreement with the conclusions of Aitken[3] concerning oxygen redistribution in mixed oxides. He showed that the heat of transport for the Rand-Markin model should be reduced by the factor $1+L_s/L_g$ when solid state diffusion is considered. L_s and L_g represent the mobilities of oxygen in the solid and gas phases, respectively, and the factor L_s/L_g is equivalent to the first term in the denominator of Eq (11).

The analysis of oxygen redistribution in the presence of a CO_2/CO mixture is formally identical to that presented above for H_2O/H_2 gases. The sole difference (aside from the numerical values of $\Delta H^\circ_{ZO/Z}$ and $\Delta S^\circ_{ZO/Z}$) is that the CO partial pressure cannot be

arbitrarily specified as could the H_2 pressure in Eq (10). The argument leading to Eq (7) is valid for CO_2/CO mixtures, but the constant value of p_{CO} cannot be greater than the CO pressure which is in equilibrium with pure carbon at the prevailing oxygen pressure. The equilibrium constant for the reaction:

$$C + \frac{1}{2} O_2 = CO \tag{13}$$

permits the maximum CO pressure to be determined from:

$$RT\ln p_{CO}^{max} = \frac{1}{2} \Delta\overline{G}_{O_2} - \Delta G^{\circ}_{CO/C} \tag{14}$$

where $\Delta G^{\circ}_{CO/C}$ is the standard free energy of formation of CO. If free carbon is present anywhere in the system, p_z in Eq (10) must be set equal to the value of p_{CO}^{max} at the axial position where this quantity is smallest, which invariably occurs at the cold end. For specified values of all parameters in Eq (10) except $p_z = (p_{CO}^{max})_{z=L}$, the calculation is performed by guessing this quantity and integrating Eq (11). The O/M profile then determines the axial variation of the fuel oxygen potential and hence $\overline{\Delta G}_{O_2}$ at $z = L$, from which $(p_{CO}^{max})_{z=L}$ may be computed by Eq (14). When this value agrees with the initial guess, the computation is complete.

Figure 3 shows the results of calculations for CO_2/CO mixtures in a fuel of average oxygen-to-metal ratio of 1.98 and b/2H = 1. Even with this very large crack size, the extent of oxygen redistribution is rather small, although the cool surface O/M has risen to nearly exact stoichiometry. The pressure of CO in the gas phase (which is the value of p_{CO}^{max} at $z = L$) is 2.6×10^{-5} atm. Since $p_{CO}^{max} > p_{CO}$ at all other positions, free carbon is present only at the

cold end of the temperature gradient. Excess carbon which may have existed in the hot region migrates to the cold end during the transient period before attainment of steady state. Since the carbon content of oxide fuels is large enough to produce CO pressures much larger than 2.6×10^{-5} atm if all impurity carbon were gasified, imposition of the temperature gradient causes extensive carbon redistribution but only minor oxygen redistribution. Had the longitudinal cracks in the fuel been smaller than the value used in constructing Figure 3, the allowable CO pressure would have been smaller and the extent of oxygen redistribution would have been reduced.

The importance of solid diffusion on the extent of oxygen redistribution depends upon the flow areas of each phase along the temperature gradient and the pressure of the "Z" component in the gas. For H_2O/H_2 mixtures in which p_{H_2} is set equal to 1 atm, rather fine cracks are required before solid state diffusion can substantially eliminate the O/M profile established by gas phase transport. With CO_2/CO mixtures as the active gas species, however, the requirement that the carbon activity nowhere exceed unity reduces the allowable CO pressure in the crack to very low values for hypostoichiometric fuels, with the result that gas phase transport of oxygen cannot build up a steep oxygen concentration gradient in the solid in the face of the leveling tendency of solid diffusion.

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FIGURE CAPTIONS

1. Fuel body with crack along the temperature gradient.

2. Effect of diffusion in the solid on oxygen redistribution and the H_2O/H_2 ratio for a fuel of average O/M = 1.96. Hot and cold temperatures are 2000°K and 1000°K, respectively. p_{H_2} = 1 atm.

3. Oxygen redistribution in a fuel of average O/M = 1.98 due to transport by a CO_2/CO mixutre. Hot and cold temperatures are 2000°K and 1000°K, respectively. (b/2H) = 1; $D^g_{CO_2}$ = 7 cm/sec at 1500°K.

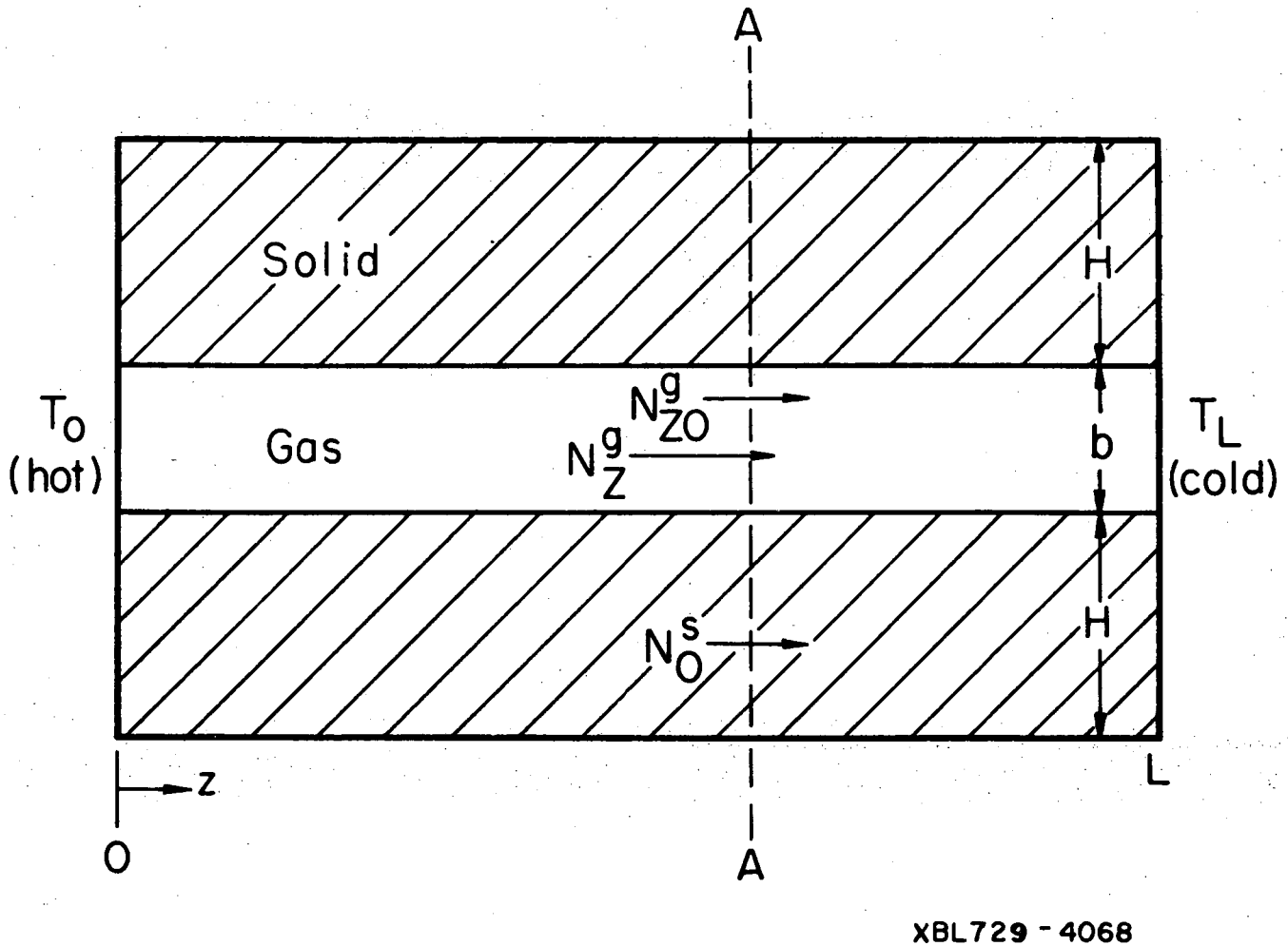

Fig. 1

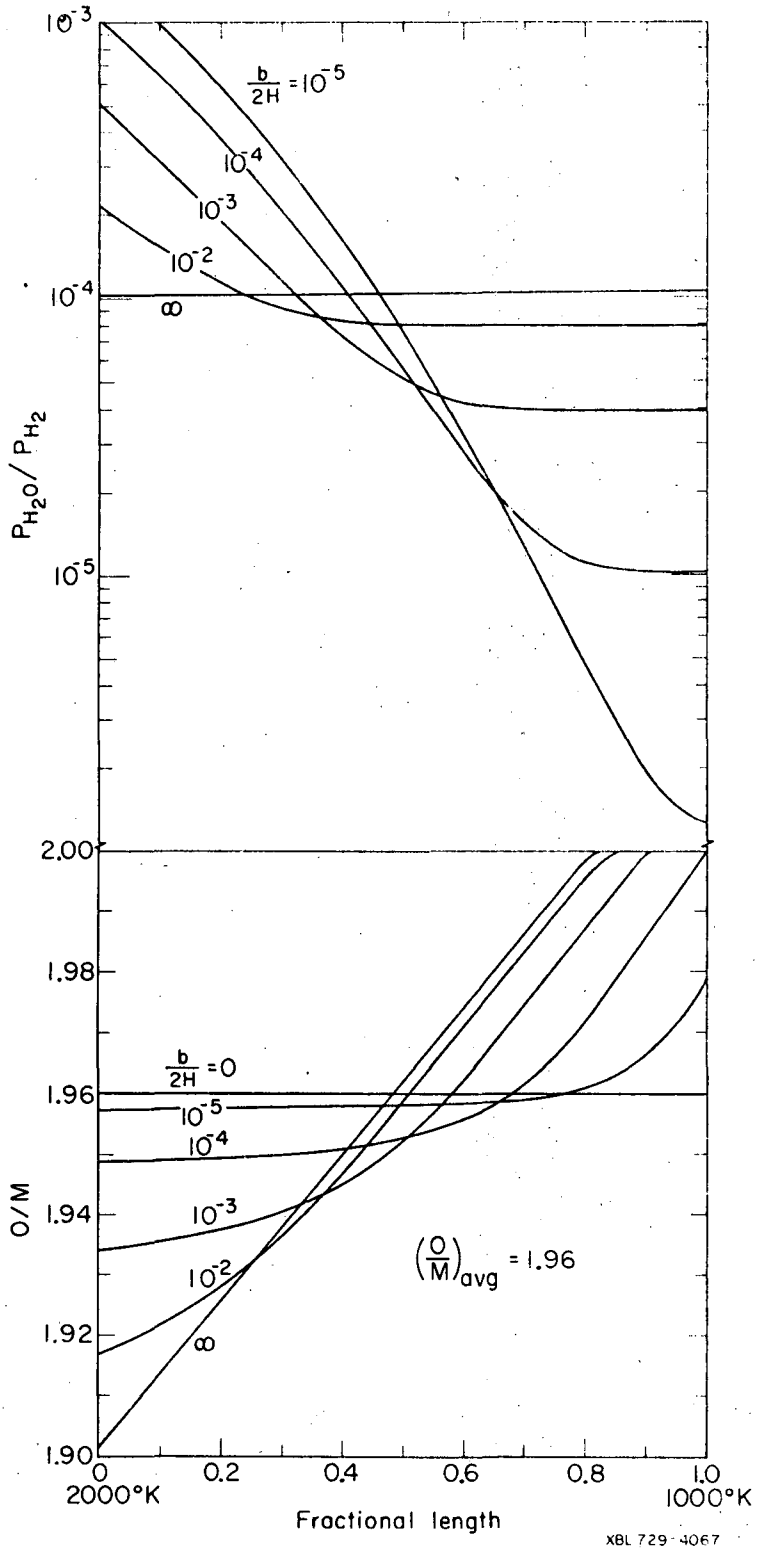
10^{-3}
10^{-4}
10^{-5}
P_{H_2O}/P_{H_2}
$\frac{b}{2H} = 10^{-5}$
10^{-4}
10^{-3}
10^{-2}
∞
2.00
1.98
1.96
1.94
1.92
1.90
O/M
$\frac{b}{2H} = 0$
10^{-5}
10^{-4}
10^{-3}
10^{-2}
∞
$\left(\frac{O}{M}\right)_{avg} = 1.96$
0
0.2
0.4
0.6
0.8
1.0
2000°K
1000°K
Fractional length
XBL 729-4067

Fig. 2

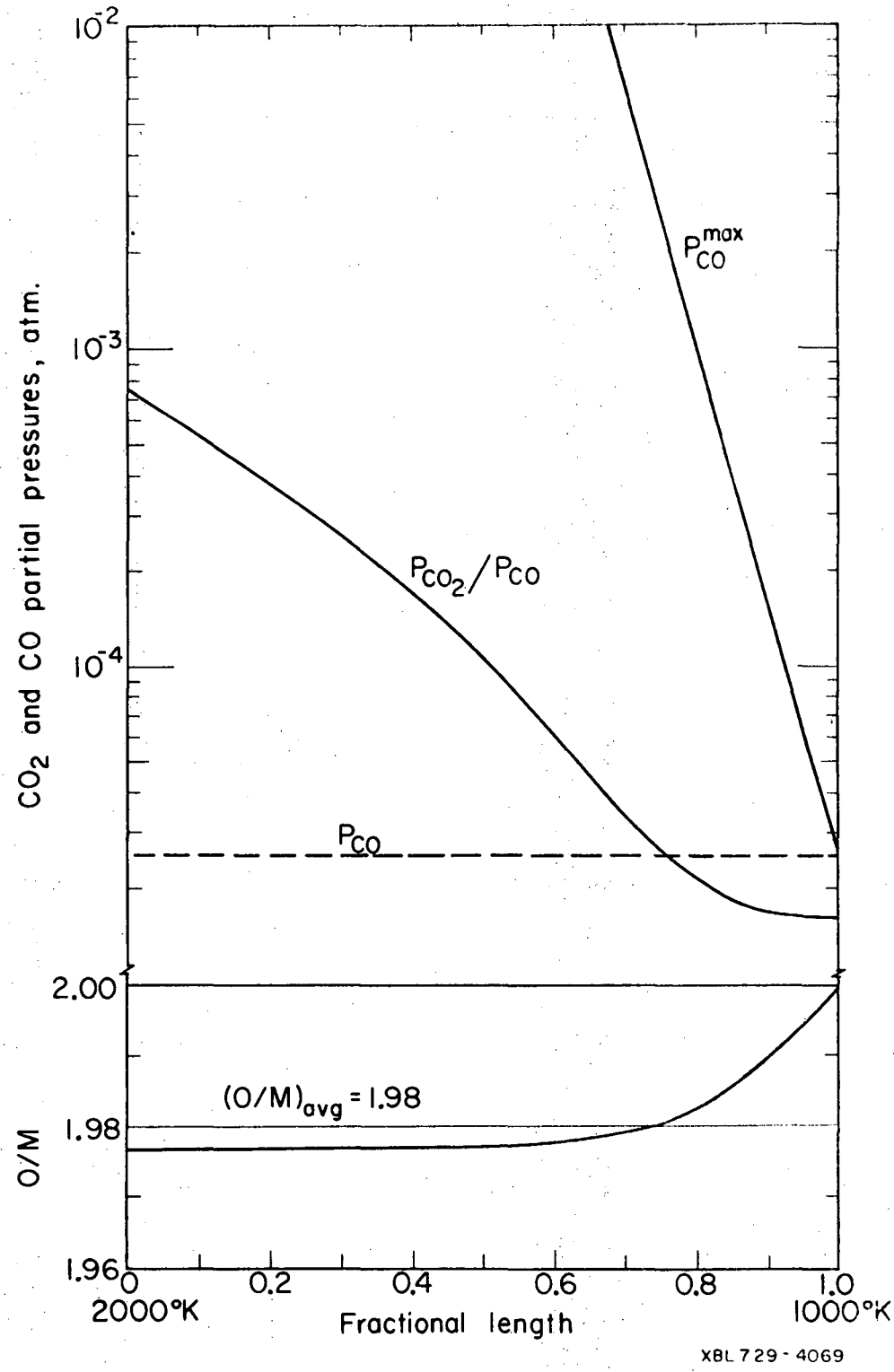
10^{-2}
10^{-3}
10^{-4}
CO_2 and CO partial pressures, atm.
P_{CO}^{max}
P_{CO_2}/P_{CO}
P_{CO}
2.00
1.98
1.96
O/M
$(O/M)_{avg} = 1.98$
0
0.2
0.4
0.6
0.8
1.0
2000°K
1000°K
Fractional length
XBL 729-4069

Fig. 3

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