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High-Temperature Heterogeneous Reaction Kinetics of Tungsten Oxidation by CO_2, CO, and O_2

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The high-temperature heterogeneous reaction rates of bulk tungsten are studied using thermogravimetric analysis in oxygen (O_2), as well as carbon dioxide (CO_2) and carbon monoxide (CO) atmospheres. Isothermal reaction rates were determined at temperatures ranging from 1300 to 1700°C. Constant system pressures of 1 atm were employed; however, O_2 and CO_2 partial pressures ranged from 0.152 to 3.8 torr and 7.6 to 64.6 torr, respectively. Using Arrhenius reaction rate kinetics, activation energies of the W–O_2 and W–CO_2 reactions were found to be 23.5 and 64 kcal/mol, whereas pressure exponents were determined to be 0.89 and 0.6, respectively. Oxidation rates were higher for O_2 than CO_2 under constant partial pressure conditions. Increasing CO concentration in the presence of constant CO_2 partial pressure was found to reduce reaction rates significantly, emphasizing the impact gas mixtures may have on heterogeneous reaction rates. The results imply chemical erosion rates of nozzles may be altered significantly by small perturbations in propellant formulations, and O_2 may play a nonnegligible role, even in very small quantities present in rocket motors.

I. Introduction

TO INCREASE the performance of future rocket motor systems, chamber pressures and temperatures will be increased well beyond current operating conditions, introducing new challenges to scientists and engineers. One of these challenges is to improve nozzle performance by reducing erosion, particularly chemical erosion (corrosion). This has led to a large increase in research over the last few years, aimed at improving the understanding of nozzle erosion so that new engineering concepts may be introduced relating to both motor and propellant design [1–5].

The bulk oxidation of refractory materials such as tungsten (W), which is a primary constituent of current and future rocket nozzle surfaces, plays an important role in the overall erosion mechanism. Therefore, a fundamental understanding of the chemical processes occurring at and below the metal surface, as well as within the nozzle fluid boundary layer, is important to the development of forthcoming nozzles which will operate at increased temperatures and pressures from today's standards. The anticipated increase in operating conditions of future rocket motors increases both physical and chemical strain on all rocket components, particularly nozzle throats, where elevated heat transfer rates may increase erosion rates, causing performance reductions and possible failure.

Rocket nozzle recession may be caused by various phenomena or mechanisms ranging from vaporization of the nozzle material, to structural failure caused by particle impact, applied pressure, or thermal stresses [6–9]. The primary erosion mechanisms of refractory metals such as tungsten, which have high melting temperatures (~3680 K for W), often stem from heterogeneous reactions at the nozzle surface forming various metal containing compounds. Many of these surface reaction product compounds exhibit vaporization and/or melting temperatures much less than that of refractory nozzle material and combustion flame temperatures. Moreover, nonadherent solid compounds may be formed at the metal surface. In these cases the compounds may be removed from the nozzle surface nearly as fast as they are formed, either by the shear forces created by high pressure gas flow, or vaporization of the compounds into the gas stream. The overall effect of these chemical mechanisms is the removal of bulk nozzle material and the expansion of the nozzle throat area, reducing overall rocket performance.

To model and understand rocket nozzle erosion, surface reaction characterization becomes a very important piece to the overall process. The majority of the reactions occurring at the surface of tungsten nozzles are oxidation reactions, which occur rapidly at high temperatures. The high-speed flows also reduce the nozzle surface boundary layers, reducing the distance which the oxidizing combustion products must be transported to adsorb and react with the nozzle material. Particularly with solid rocket motors, fuel rich conditions exist and the primary oxidizing species of nozzles are CO_2, H_2O, CO, OH, O, and NO. Determination of fundamental reaction kinetics of basic reactions including the oxidizers above is the first step in building a reaction mechanism. Although heterogeneous reaction kinetics of individual species are often affected by the presence of other species, understanding the individual kinetics provides an elementary framework to build more complex models. To date there has been several studies of gas–solid surface reaction kinetics of bulk tungsten at high temperature, with most involving the reaction of tungsten and molecular oxygen (O_2) [10–15]. Less work has been done with other compounds such as CO_2 [16,17], H_2O [18–21], O [22], or nitrogen containing compounds [23], and even less has looked into how mixtures of these compounds may affect overall reaction rates [16,24,25]. Most of this work presents a phenomenological perspective of oxidation rates, which may not be adequately applied to modeling and prediction of kinetic rates. This limited pool of available kinetic data has restricted development of new models used to predict nozzle erosion rates [5].

Most high-temperature oxidation reactions occur fairly rapidly, consuming reactants and creating a concentration gradient between the surrounding gas and the surface. If the diffusion time scale of the reactant to the metal surface is not at least as fast as the chemical reaction time scale, apparent reaction kinetics may be considerably different from the true chemical reaction kinetics [26]. In static reactor experiments, which are used in most of the previous studies of high-temperature oxidation kinetics, apparent rates, activation energies, and reaction orders are often different from true values unless the diffusional limitation is recognized and treated accordingly.

In the case of tungsten oxidation at high temperatures, the oxides are vaporized as fast as they are formed, and the rate of oxidation follows a linear rate law, which increases exponentially with

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temperature. Because nonadherent oxides are formed, the oxidation rates may be kinetically limited by surface collision rates, surface species dissociation or migration, and/or surface desorption processes. As the concentration of oxidizing molecules is increased, so are the rates of collision, increasing the overall oxidation rate until at very high concentrations the surface becomes saturated with oxidizing molecules and the rate becomes independent of concentration [12]. At lower pressures, the linear rate law is a function of both pressure and temperature, as described by the Arrhenius rate equation:

$$k_i(T, P) = A_i \cdot \exp(-E_i/Ru \cdot T_s) \cdot P_i^{n_i} \quad (1)$$

where k (units of $\mathrm{W} \cdot \mathrm{cm}^{-2} \cdot \mathrm{s}^{-1}$) is the reaction rate, A is the preexponential factor, E is the activation energy, Ru is the universal gas constant, T_s is the W surface temperature, P is the oxidizer partial pressure, n is a pressure exponent, and the subscript i refers to the oxidizing species (i.e., O_2 or CO_2).

This paper presents results on the high-temperature heterogeneous reaction kinetics of tungsten in the presence of O_2, CO_2, and CO. Reactions involving CO_2 and CO have been studied previously [16,24]; however, the work by Walsh et al. [16] is the only study in which rates have been characterized as a function of temperature and pressure and presented quantitatively in mathematical form. Because CO_2 and CO are primary product species in solid propellant rocket motor nozzles, a detailed understanding of the heterogeneous reaction kinetics is required to improve modeling capabilities and accuracy. The oxidation rates of W by O_2 are studied and presented as well. Although O_2 is not generally a primary species in rocket exhausts, it provides a simple system for experimental validation, while increasing the knowledge base of fundamental high-temperature refractory metal oxidation. The implications of these results are discussed in relation to the corrosion of rocket nozzles as well.

II. Experimental Approach

The oxidation kinetics of bulk tungsten were obtained under isothermal conditions by measuring the weight change over time using a thermogravimetric analyzer (TGA) developed at The Pennsylvania State University. The primary components of the TGA are a Cahn D-101 digital recording balance, capable of measuring changes in mass as low as 1 μg, an Applied Test Systems vertical tube furnace, which has a maximum temperature of 1700°C, and several Teledyne Hastings mass flow controllers (200 series) to regulate the flow of each gas to within $\pm 1\%$. A schematic of the TGA system is shown in Fig. 1. Test samples of tungsten foil were cut from 99.95% W foil obtained from Goodfellow (W 000315). Originally, 25-μm-thick foils were used but were too thin, reducing the number of test runs which could be completed before appreciable changes in surface areas occurred. Subsequent tests have used 200-μm-thick foils, which have shown to erode fairly uniformly, maintaining an overall rectangular shape during testing. Dimensions are, however, slightly reduced during testing and slight tapers have been found at the leading edge, due to flow stagnation and boundary-layer development. These small changes in sample dimensions were estimated during testing using the mass loss of tungsten from each test run. The maximum change in sample surface area was found to be 15%, spread over 29 runs; therefore, each run was assumed to take place at a constant surface area. Although samples of various dimensions have been used, varying from 1.5 to 2.8 cm^2, most testing was completed using 8.35×16.25 mm foil samples; testing indicated reaction rates ($\mathrm{g}/\mathrm{cm}^2 \cdot \mathrm{s}$) of various sample sizes were within experimental uncertainties of each other [27]. Because of difficulties in shearing the 200 μm foils, electrical discharge machining (EDM) was used to cut the samples. This method not only allowed for very smooth cuts to be made, but enabled precise dimensions to be held.

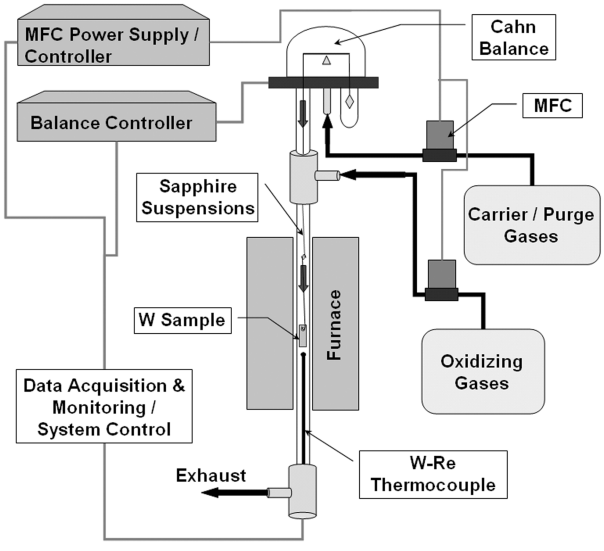

Fig. 1 Schematic of TGA used for determination of heterogeneous reaction kinetics.

The high temperatures, oxidative atmospheres, and time scales of testing restricted the pool of materials which could be used within the system. To control the atmosphere within the furnace, a high purity alumina reaction tube (0.875 in outer diameter, 0.625 in inner diameter) was used. The tube was sealed directly to the balance and gas connections using O-rings to eliminate leaks in the reaction system. The tungsten samples were suspended from the microbalance into the furnace by sapphire suspensions produced by Photran, LLC (Poway, California). The sapphire suspensions were required because of their high-temperature performance, ductility, strength, and chemical inertness in oxidative atmospheres. Small holes ($\sim$1 mm) were cut into the samples using a carbide bit so they could be hung from the suspensions. To minimize the reaction of tungsten during system heating, pre- and postruns, ultrahigh purity inert gases were used (99.999%). During heating to the desired test temperature hydrogen (H_2) was flowed through the TGA to clean the metal surface of oxides or other impurities and limit oxidation by trace impurities in the gas stream. All tests were conducted using helium (He) as the carrier gas, which kept oxidative gas concentrations low and protected the balance from chemical attack. Further purification was accomplished by running the H_2 and He gases through copper coils submerged in liquid nitrogen to condense H_2O and O_2, removing them from the gas flow. The system temperature adjacent to the tungsten sample was monitored using a type-C (W-Re) thermocouple, which has an accuracy of $\pm 1.0\%$. The thermocouple was protected from chemical attack by a high purity alumina tubewell.

Once the desired system temperature was reached, the system was allowed to stabilize for a minimum of 15 min before testing. During all tests, system flow rates, temperature, mass, and time were recorded using a National Instruments data acquisition card (NI PCI-6014) used in cooperation with a LabVIEW interface program. LabVIEW also allowed for simultaneous control of the flow rates using up to four different mass flow controllers (MFCs) through the MFC power supply (Teledyne Hastings THPS-400). All test information was recorded at a sampling rate of 1 Hz, which was the maximum sampling rate set by the communication with the Cahn balance. Tests lasted as little as 20 s in duration to more than 3 min, depending on the oxidizer type, concentration, and temperature. The reaction rates were determined by the slope of the mass loss curve over time ($\mathrm{d}m/\mathrm{d}t$); in most cases a least-squares fit of the data produced R^2 values greater than 0.999. No cases were found which did not produce a linear mass loss curve.

Diffusion limited reactions were eliminated or reduced to negligible levels in the TGA by using high volume flows. To determine the required flow rates to create kinetically limited conditions, temperature and oxidizer concentration were kept constant while increasing flow rate. As flow rates approach kinetically limited conditions, reaction rates (i.e., W mass loss rate) become independent of flow rate. Because of high reaction rates between W and O_2, diffusion limited reactions were found at the

maximum system temperature and flow rate, reducing the temperature range of the applicable kinetic data. In the case of the W and CO_2 reaction, kinetically limited reactions were found over the entire temperature range using a system flow rate of 7 SLPM (standard liters per minute, $P_{std} = 760$ torr, $T_{std} = 0°C$). Examples of raw data and the testing used to determine kinetically controlled conditions are presented elsewhere [27].

III. Results and Discussion

The results of these oxidation studies are presented in the following sections for varying temperatures and partial pressures of the subject species, followed by a corollary discussion of the effects of nozzle erosion rates under rocket motor conditions. Results of oxidation kinetics are compared and contrasted with previous literature as well.

A. Oxidation Kinetics in Presence of O_2

The oxidation rate of bulk tungsten in the presence of molecular oxygen was studied at partial pressures between 0.152 and 3.8 torr (0.02–0.51 kPa or 0.02–0.5%). The overall oxidation rates were found to be fast and therefore, at the highest temperatures considered, diffusion limited reactions were found, as indicated by the onset of what appears to be temperature independent or inversely dependent reactions at high temperatures in Fig. 2. A maximum reactor flow rate of 17 SLPM was used; larger flow rates were not used due to concerns of reducing the sample temperature. To determine the activation energy of the tungsten and oxygen heterogeneous reaction (E_{O_2}), the highest temperatures were neglected (>1875 K) determining E_{O_2} to be 22.6 kcal/mol of tungsten on average, with a standard deviation of 1.4. This activation energy is within the range of values found by previous researchers (14.3–48 kcal/mol) as shown in Table 1. However, many of these studies involved either lower temperatures or static flow conditions. The work by Walsh et al. [15] is the only study in which high flows were used to remove diffusion limited reactions at very high temperatures, determining the activation energy to be 23 kcal/mol, nearly the exact value determined in this study.

The oxygen pressure dependence on the reaction rate was determined from the slope of constant temperature data when plotting $\ell_n(k_{O_2})$ verse $\ell_n(P_{O_2})$, yielding a pressure exponent (n_{O_2}) of 0.90 with a standard deviation of 0.01. Tests determining this pressure exponent were conducted in the same session using the same sample, thus minimizing errors. Oxygen partial pressures used ranged from 0.152 to 3.8 torr during these tests. The pressure exponent of near unity indicates a reaction rate nearly proportional to the collision frequency of oxygen molecules with the bulk surface, and is not rate limited by the desorption of volatile oxides, or O_2 dissociation at the surface. Other researchers have found pressure exponents as high as 1.35 [28] and as low as 0.55 [13]. Much of the previous literature does not report a pressure exponent.

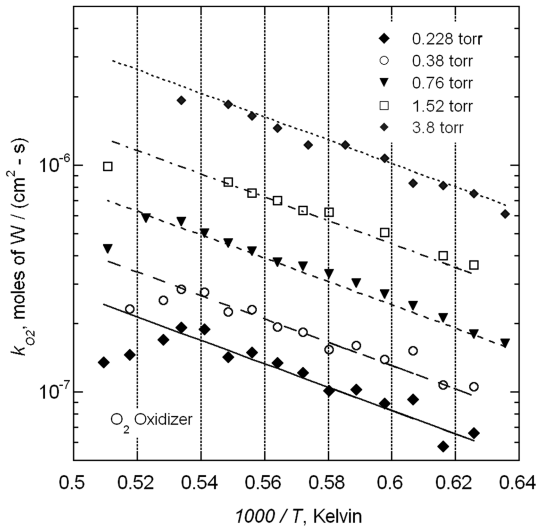

Fig. 2 Rates of tungsten consumption by O_2 [lines from Eq. (2)].

Using the pressure dependence of the W–O_2 oxidation reaction derived prevously, the Arrhenius reaction rate preexponential factor (A_{O_2}) was estimated by manipulation of Eq. (1), plotting the $\ell_n(k_{O_2}/P_{O_2}^n)$ vs $1/T$, where A_{O_2} is the y-axis intercept. These results provide an initial estimate of an appropriate analytical model of tungsten oxidation by O_2; however the model was refined within the range of uncertainty, increasing accuracy of predictions with the majority of data. This model is shown in Eq. (2). The oxidation rates predicted by this correlation are shown in Fig. 2, where the molecular weight of tungsten is 183.84 g/mol. The derived Arrhenius rate function predicts measured rates within acceptable limits of error, as most of the data is within ±10%, and all is within ±20% ($1572 < T < 1875$ K):

$$k_{O_2} = A_{O_2} \cdot \exp\left[\frac{-E_{O_2}}{Ru \cdot T_s}\right] \cdot [P_{O_2}]^{n_{O_2}}$$
$$= 3.8 \times 10^{-4} \frac{\text{mol of W}}{\text{cm}^2 \cdot \text{s} \cdot \text{torr}^{0.89}} \cdot \exp\left[\frac{-23.5\,\frac{\text{kcal}}{\text{mol}}}{Ru \cdot T_s}\right] \cdot [P_{O_2}]^{0.89} \quad (2)$$

B. Oxidation Kinetics in Presence of CO_2 and CO

The oxidation rate of bulk tungsten in the presence of carbon dioxide was studied at partial pressures between 7.6 and 64.6 torr (1.01–8.61 kPa or 1.0–8.5%). As expected, based on previous literature, no measurable tungsten oxidation was found with carbon monoxide alone. The overall oxidation rates were also found to be slower than found with O_2, and therefore overall reactor flow rates of 7 SLPM were found to produce kinetically limited reaction rates at all temperatures considered. Oxidation rate results at various CO_2 partial pressures are shown in Figs. 3 and 4. Fitting the results of these figures to the Arrhenius expression [Eq. (1)], the activation energy (E_{CO_2}) of the W–CO_2 reaction is determined to be on average 63.6 kcal/mol of reacted tungsten, with a standard deviation of 2.6 kcal/mol. This activation energy is nearly triple that of the O_2 oxidation reaction, indicating a much greater energy barrier in forming a gas phase tungsten oxide from CO_2. This activation energy is lower than 79 kcal/mol, which is the value found by Walsh et al. [16]. A summary of the previous reaction kinetics studies of W and CO_2 is shown in Table 2. The work by Harvey [17] involves solely diffusion limited reactions.

The carbon dioxide pressure dependence on the oxidation rate was determined using the same procedure as with the W–O_2 system, determining the pressure exponent (n_{CO_2}) to be 0.60 with a standard deviation of 0.03. The pressure dependence, which is much less than unity, indicates a desorption or dissociation limited reaction. The limiting dissociation process could be due to the dissociative adsorption of CO_2 into CO and O. A limiting desorption process may be due to formed CO, or a volatile tungsten oxide. Detailed modeling is required to resolve the dominant or limiting reaction routes.

Using the pressure dependence of the W–CO_2 oxidation reaction, the Arrhenius reaction preexponential factor (A_{CO_2}) was estimated using the same graphical plotting procedure discussed previously. As with the previous system, these results provided an initial estimate of an appropriate analytical model of tungsten oxidation by CO_2. With refinement, an empirically derived analytical kinetic model for tungsten oxidation by CO_2 was developed, shown in Eq. (3). Most of the data of Figs. 3 and 4 lay within ±15% of the Arrhenius fit, and nearly all data were within ±20%:

$$k_{CO_2} = A_{CO_2} \cdot \exp\left[\frac{-E_{O_2}}{Ru \cdot T_s}\right] \cdot [P_{CO_2}]^{n_{CO_2}}$$
$$= 0.285 \frac{\text{mol of W}}{\text{cm}^2 \cdot \text{s} \cdot \text{torr}^{0.67}} \cdot \exp\left[\frac{-64\,\frac{\text{kcal}}{\text{mol}}}{Ru \cdot T_s}\right] \cdot [P_{CO_2}]^{0.6} \quad (3)$$

Although carbon monoxide was found to produce no measurable oxidation rates using the TGA, CO was found to affect oxidation

Table 1 Summary of previous W–O_2 high-temperature kinetics studies

Authors, yr	System pressure, torr	System Temp., °C	Partial O_2 pressure, torr	Experimental method	E, kcal/mol	Pressure exponent, n	Author comments/ conclusions
Baur et al., 1956 [10]	(assumed = P_{O_2})	1107–1627	1034-25,840	TGA ($\Delta m/\Delta t$), static flow furnace	48	——	WO_2 and WO_3 products found
Gulbransen & Andrew, 1960 [11]	<760 (assumed = P_{O_2})	500–1300	1–76	TGA ($\Delta m/\Delta t$), static flow furnace	32.5	——	Rate limited by WO_3 volatility, diffusion of O_2 and W_3O_9 products, mass loss @ $T >$ 1200°C
Perkins & Crooks, 1961 [12]	1–40	1300–3000	0.21–8.4 (assuming 21% O_2 in air)	Surface recession ($\Delta x/\Delta t$), static flow, resistively heated sample	31.5 (1300–1750°C)	0.62 (1300–1750°C)	Above 1750°C the reverse reaction rate (dissociation of WO_3 on surface) becomes important and decreases reaction rate
Gulbransen et al., 1964 [14]	(assumed = P_{O2})	1150–1615	2–100	TGA ($\Delta m/\Delta t$), static flow furnace	14.3	1.1	~13% of O_2 molecules colliding w/surface react (i.e. sticking factor = 0.13)
Bartlett, 1964 [13]	<760 (assumed = P_{O2})	1320–3170	0.00076–760	Surface recession ($\Delta x/\Delta t$), resistively heated sample	42	0.55–0.8	Above 2000°C reaction probabilities were 0.06 @ all pressures and reaction rate was independent of T, multilayer kinetic process suggested forming WO_2 and WO_3
Walsh et al., 1967 [15]	2–11.1 (static)	1727–3027	0.11–11.5 (stagnation)	Surface recession [$\Delta(x_f - x_i)/\Delta t$], high velocity jet impingement, inductively heated sample	23	——	Diffusion limited rates found at highest temperatures
Harvey, 1973 [28]	600	2177–2927	0.012–0.09	Mass change [$\Delta(m_f - m_i)/\Delta t$], static flow, resistively heated sample	——	1.10–1.35	Reaction rates at constant O_2 partial pressure decreased w/ increasing T in this diffusion limited system

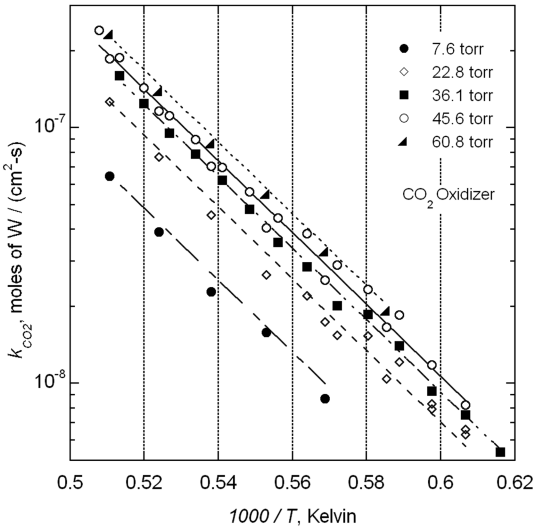

Fig. 3 Rates of tungsten consumption by CO_2 [lines from Eq. (3)].

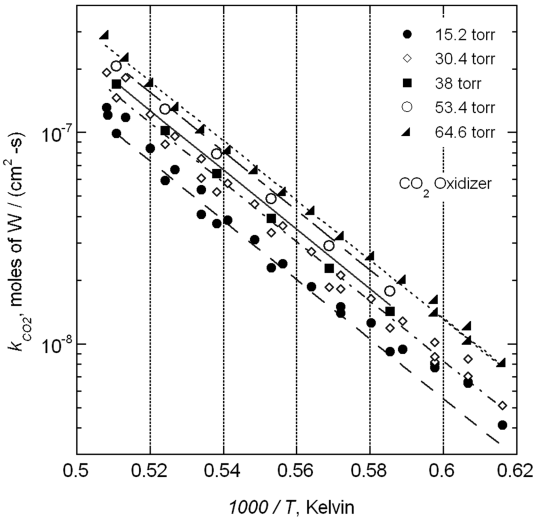

Fig. 4 Rates of tungsten consumption by CO_2 [lines from Eq. (3)].

rates of CO_2 considerably. This effect was observed previously by other researchers [16,24], however Walsh et al. [16] have been the only research group to quantify the effect of CO on the oxidation rates of CO_2 as a function of temperature and pressure. The effects of the CO addition on CO_2 oxidation rates were determined at a constant partial pressure of 34.2 torr, and CO to CO_2 ratios up to 4

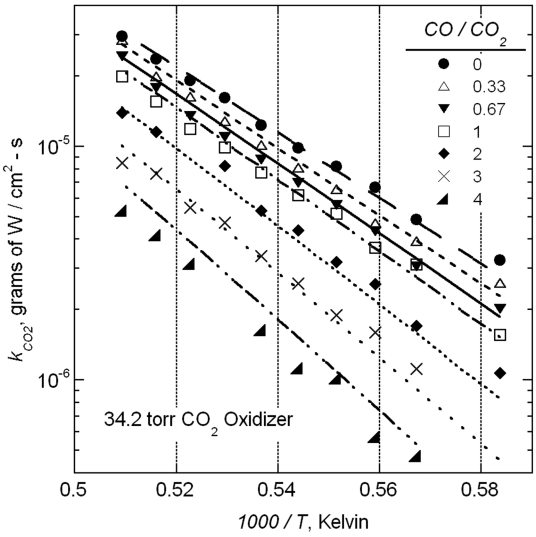

Fig. 5 Effect of CO on the CO_2 oxidation rates of tungsten [lines from Eq. (4)].

(Fig. 5). The plot shows that although the CO does not cause the consumption of bulk tungsten, it does significantly affect the oxidation rates involving CO_2. The activation energy of the W–CO_2 reaction is affected by the addition of CO as well. Curve fitting of the data in Fig. 5 illustrated activation energies of 59.1, 63.5, 65.7, 63.3, 70.7, 71.1, and 85.1 kcal/mol at ratios of 0, 0.33, 0.67, 1, 2, 3, and 4, respectively, indicating stronger temperature dependence when a large amount of CO is present. Up to a ratio of unity, activation energies are within experimental error of each other, signifying that the CO does not change the limiting reaction steps in the overall mechanism. However, at high ratios it seems clear that CO alters the limiting reaction steps.

To better quantify the effect of CO on the rates of oxidation involving CO_2 and W, Fig. 6 was created and an empirical correlation was applied to the data [Eq. (4)]. The results indicate that reaction rates are significantly affected by CO, even at ratios less than 0.33. These figures illustrate a temperature dependent pattern relating to the CO addition. As a caveat, this correlation is a greatly simplified approach for describing the presence of CO on the overall reaction rates and therefore contains a great deal of empiricism.

The abilities of the empirical correlations to predict the kinetic reaction rates of tungsten oxidation are shown in Figs. 3–5 in the form of solid and dashed lines. The correlations perform well over the range of conditions in this study. Walsh et al. developed a similar equation, however; in their correlation the effect of CO is magnified with increasing temperature [see Eq. (5)] [16]. Using Eq. (5), the experimentally derived reaction rates of this study are under-predicted. However, the greater activation energy and pressure

Table 2 Summary of previous W–CO_2 high-temperature kinetics studies

Authors, yr	System pressure, torr	System temp., °C	Partial CO_2 pressure, torr	Experimental method	E, kcal/mol	Pressure exponent, n	Author comments/conclusions
Walsh et al., 1967 [16]	300 (static)	1927–3027	20–337 (stagnation)	Surface recession $[\Delta(x_f - x_i)/\Delta t]$, high velocity jet impingement, inductively heated sample	79	0.88	Diffusion limited rates found @ high T (>2377°C), small CO additions showed depressed rates, overall rates much less than O_2
Harvey, 1974 [17]	600	2177–2727	0.0162–0.097	Mass change $[\Delta(m_f - m_i)/\Delta t]$, static flow, resistively heated sample	——	0.78–1.18	Diffusion limited rates found throughout

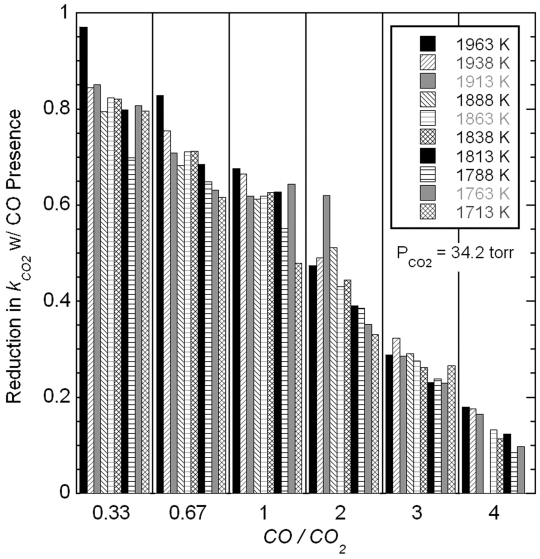

Fig. 6 Reduction in tungsten oxidation rate by CO_2 as function of CO:CO_2 ratio.

dependence causes Eq. (4) to underpredict the experimental data presented by Walsh et al. If the correlation to correct for CO and CO_2 mixtures developed by Walsh et al. is applied to Eq. (3), the reaction rates found in this study are overpredicted, as the calculated results indicate a CO_2 reaction rate reduction of less than 28% at the highest temperature (i.e., 1973 K) and CO concentration (i.e., $4 \cdot$ CO:CO_2) studied, compared to 77% in this study. In addition to studying two different temperature ranges, two significantly different experimental apparatuses were used in these studies. Walsh et al. used a stagnation flow reactor, where an inductively heated sample was oxidized with a stagnating flow of a known reactive mixture. The reactive mixture is applied for a given period of time and the sample recession is recorded by measuring pre- and post-test conditions. Additionally, total system pressures in the tests by Walsh et al. were less than 1 atm:

$$k_{CO_2/CO} = A_{CO_2} \cdot \exp\left[\frac{-E_{CO_2}}{Ru \cdot T_s}\right] \cdot [P_{CO_2}]^{n_{CO_2}} \cdot \exp\left[-(2.194 \times 10^{11} \cdot T^{-3.574}) \frac{P_{CO}}{P_{CO_2}}\right] \quad (4)$$

$$k_{CO_2/CO}(\text{Walsh et al.}) = 2.19 \cdot \exp\left[\frac{-79\ \text{kcal/mol}}{Ru \cdot T_s}\right] \cdot [P_{CO_2}]^{0.88}\left[1 - 0.547(P_{CO}/P_{CO_2}^{0.5})^{0.88} \cdot \exp\left[\frac{-14.7\ \text{kcal/mol}}{Ru \cdot T_s}\right]\right] \quad (5)$$

The reduction in tungsten oxidation rates by CO_2 with the introduction of CO may be caused by several mechanisms. The first is a function of the experimental conditions. At very high temperature, CO_2 will dissociate into CO, O, and O_2. The addition of CO into a mixture of CO_2 will reduce the levels of dissociation at equilibrium. Using CHEMKIN 4.0 [29] the dissociation kinetics were modeled to determine how fast CO_2 dissociates under experimental conditions. The results showed that CO_2 will indeed dissociate into O_2 and O, which would increase reaction rates found using the TGA. At the highest temperatures considered, equilibrium concentrations of O_2 and O would cause severe increases in oxidation rates. However, negligible dissociation occurs at temperatures below 1400 K [30] and kinetics indicate that equilibrium conditions cannot be met given the time interval for dissociation of the CO_2 within the furnace before reaching the test sample. Time intervals of 50–150 ms have been estimated, given a constant flow rate (7 SLPM) and varying reactor temperatures. In fact, calculations would indicate that changes in CO_2 reaction rates due to O_2 formation were less than 10% at 2000 K and 0.5% at 1750 K, with no CO addition. When there is twice as much CO in the system than CO_2, changes are less than 0.5% at 2000 K. This variation is deemed acceptable given uncertainty in kinetic data and also verifies that the presence of CO directly affects the CO_2 oxidation rate. Additionally, results indicate a stronger CO influence at lower temperatures, supporting the fact that dissociation may not explain the reaction rate reduction. Moreover, if the dissociation of CO_2 were playing a significant role, reaction rates would increase dramatically at the highest temperatures studied when no CO is present. This result indicates that although dissociation of reactive gases should be considered in any experimental apparatus measuring reaction rates, it does not significantly affect CO_2 reaction rates found here, particularly at lower temperature, or in cases where CO is added to the gas mixture.

Another explanation for the reduction in reaction rates with CO addition are reductions in the net desorption rates of CO from the bulk surface, reducing available adsorption or dissociation sites for CO_2, essentially reducing available surface area for reaction. Figure 7 helps explain this point, which illustrates several greatly simplified reactions. In reactions 1–5, as the CO partial pressure increases each reaction is driven increasingly in the direction of decreased partial pressure. This can either reduce reactive surface sites through CO adsorption (reactions 1 and 5), or decrease the net rate of CO_2 dissociation (i.e., decrease O-atom production, reactions 2–4); each in turn reduces rates of tungsten surface atom volatilization. Reactions 2 and 3 basically illustrate the same reaction; however, one creates a surface species tungsten dioxide, the other a gas phase species. Reactions 1 and 5 illustrate the nondissociative and dissociative CO adsorption processes, respectively. This shift in equilibrium has been used in the past as the primary explanation for reductions in the CO_2 oxidation rates with CO addition [24].

Based on the results of a recent theoretical study conducted by Chen et al. involving the adsorption of CO_2 and CO on a W(111) surface, the most likely scenario occurring is that dissociative adsorption (reactions 5 and 6) poisons the surface oxidation process [31]. The W–C bonding at the surface is calculated to be stronger than all other bonds at the surface (i.e. W–CO_2, W–CO, W–O) and highly resistant to desorption or surface diffusion processes. Therefore, the additional carbon present at the surface due to dissociative adsorption of CO effectively reduces the available surface area for oxidation. The study of Chen et al. also estimated the kinetics of the adsorption processes. The dissociative adsorption rate of CO is predicted to be approximately 2 orders of magnitude slower than CO_2 adsorption; however, this does not account for desorption processes. Although the initial process of CO_2 adsorption may occur faster, equilibrium surface concentrations of carbon atoms at the surface should quickly be approached. The results of this study are supported by other studies involving CO adsorption on W(111) surfaces [32,33]. These studies indicate that CO oxidation is a self-poisoning process as the W–C bonding restricts dissociative

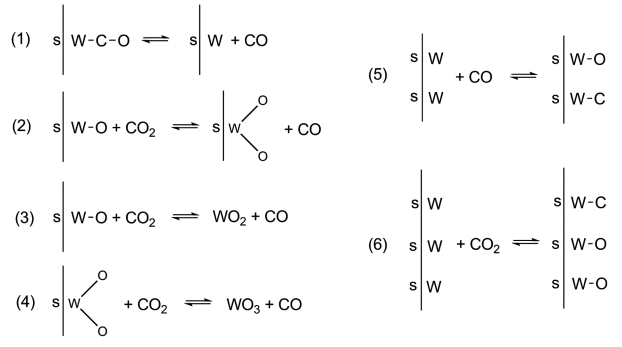

Fig. 7 Surface mechanisms containing CO which may affect oxidation rates.

adsorption of CO, thereby limiting the extent of oxidation and not allowing higher oxides to form which could dissociate, leading to corrosion or mass loss of the tungsten substrate. The kinetics also indicate a minimal activation energy for the adsorption reactions, which when compared to the global oxidation reaction energies found in the current study indicates a surface reaction or desorption limited reaction.

At this time there is some debate as to what the primary tungsten oxide desorption species is, although nearly all work points toward a mixture of WO_2 and WO_3 [34–36]. Mass-spectrometric studies of tungsten oxidation by O_2 ranging in temperatures from 1400–3150 K indicate that at lower temperatures WO_3 or one of its polymers are the primary desorption species, whereas at the highest temperatures WO_2 is the dominant species. No previous studies have been located which determined if oxidizers such as H_2O, OH, CO_2, or NO affect the types of species vaporizing from an oxidizing tungsten surface. Although all studies involving this subject consider high-temperature conditions, evacuated environments are needed for spectroscopic measurements, and therefore none consider high pressure conditions such as present in the TGA, or a rocket motor. Experimental determination of desorption species under high temperature and pressure conditions is extremely difficult, as in situ methods are needed. In the past, researchers have relied on the chemical analysis of the solid oxides condensed in lower temperature regions, where chemical composition of tungsten oxides may differ significantly from that of the desorbing species. Most of the oxides formed on TGA tube walls and the thermocouple protection tube are a combination of purple, blue, and brown, indicating oxides of $WO_{2.9}$ (blue) and WO_2 (brown). As pressure increases, it may be assumed that the primary desorption species will shift toward the higher oxide, WO_3.

C. Nozzle Corrosion Reactions and Rates

Molecular oxygen is generally viewed as playing a small and often negligible role in the oxidation rates of tungsten based rocket nozzles due to fuel rich conditions. Carbon dioxide and monoxide, however, are primary product species of solid rocket propellants which use hydrocarbon based fuels and binders. To explore the effects of these rates on nozzle erosion, a simple, nonaluminized ammonium perchlorate (AP) and hydroxyl-terminated polybutadiene (HTPB) propellant is considered. Using NASA Chemical Equilibrium with Applications (CEA) software [30], the equilibrium mole fraction of combustion product species is considered, as well as quasi-equilibrium mole fractions of nozzle boundary-layer species, assuming bulk tungsten as the primary component (Table 3). Using the equilibrium combustion product mole fractions, the kinetically limited throat recession rate may be estimated based on the CO_2, CO, and O_2 pressures, and extrapolation of the previously developed equations to higher temperature ranges (see Fig. 8). Nozzle surface temperatures are estimated to be 400 K less than equilibrium. The results, considering each oxidizer individually, yield recession rates (r_c) ranging from approximately 3–26 μm/s, and illustrate the significant role CO plays in reducing the CO_2 oxidation rates. Also

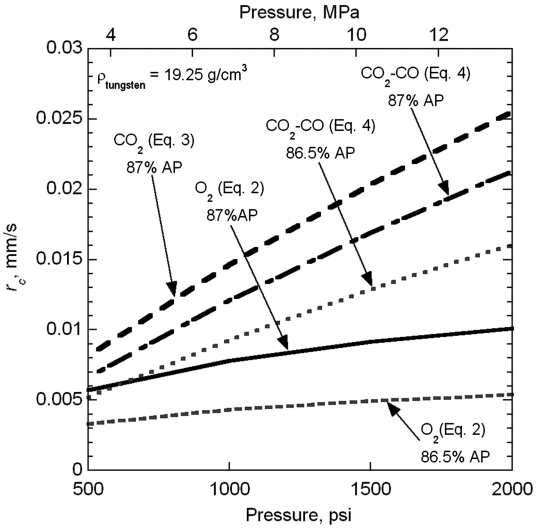

Fig. 8 Estimation of kinetically limited corrosion rates of a tungsten nozzle due to individual oxidizing species.

shown is the effect of changing propellant formulations or stoichiometry. A shift in 0.5% in mass of the propellant mixture causes rather significant changes in the estimated recession rates. The change in the O_2 related recession rate is proportional to the change in O_2 partial pressure in the product gas stream; however, the increased CO:CO_2 ratio due to increased HTPB concentration causes a nonproportional change in the CO_2 related recession rate. These results would also indicate that even in minute quantities, O_2 may create an appreciable amount of corrosion within a rocket motor due to high pressure conditions and may not be immediately neglected without consideration. It is also interesting to note that the calculated specific impulse of these two propellant formulations changes less than 0.1%.

Table 3 shows that the primary oxidizing species, in terms of overall partial pressures, are H_2O, CO_2, and OH. Hydrogen chloride (HCl) is present in significant quantities as well, but has been shown to produce little to no erosion of bulk tungsten [18,24], although the presence of chlorine (Cl_2) has been found to increase tungsten oxidation rates of O_2. Rosner and Allendorf [25] determined that when Cl_2 is added to a constant O_2 pressure mixture, ablation rates of tungsten are significantly increased, as the primary oxide product is shifted to WO_2Cl_2 or some other tungsten oxychloride. Similar to the case of CO_2 and CO, the addition of H_2 to a constant pressure H_2O mixture has been found by Olcott and Batchelor [24] to reduce oxidation rates. These conclusions, in addition to the results of this study and Walsh et al. [16], all demonstrate that heterogeneous tungsten oxidation rates are significantly affected by gas mixture constituents and relative concentrations. Individual system kinetics may not be used to accurately predict reaction rates of multi-component systems using "additive" or other simplified techniques.

Table 3 Equilibrium combustion and boundary-layer species using a nonmetallized AP-HTPB propellant and tungsten nozzle

87% AP − 13% HTPB (mass) P = 1000 psi = 6.89 MPa T_{equil} = 2946 K		86.5% AP − 13.5% HTPB (mass) P = 1000 psi = 6.89 MPa T_{equil} = 2909 K	
Primary combustion species	Primary boundary-layer species	Primary combustion species	Primary boundary-layer species
$Y_{H_2O} = 0.395$	$Y_{W(cr)} = 0.320$	$Y_{H_2O} = 0.385$	$Y_{W(cr)} = 0.322$
$Y_{HCl} = 0.180$	$Y_{H_2} = 0.155$	$Y_{HCl} = 0.178$	$Y_{H_2} = 0.150$
$Y_{CO} = 0.135$	$Y_{H_2O} = 0.152$	$Y_{CO} = 0.148$	$Y_{H_2O} = 0.156$
$Y_{CO_2} = 0.104$	$Y_{CO} = 0.145$	$Y_{CO_2} = 0.099$	$Y_{CO} = 0.136$
$Y_{N_2} = 0.093$	$Y_{HCl} = 0.081$	$Y_{N_2} = 0.092$	$Y_{HCl} = 0.080$
$Y_{H_2} = 0.069$	$Y_{WO_2(OH)_2} = 0.032$	$Y_{H_2} = 0.080$	$Y_{WO_2(OH)_2} = 0.036$
$Y_{Cl} = 0.009$	$Y_{WO_2Cl_2} = 0.023$	$Y_{Cl} = 0.006$	$Y_{WO_2Cl_2} = 0.025$
$Y_{OH} = 0.008$	$Y_{CO_2} = 0.019$	$Y_{OH} = 0.007$	$Y_{CO_2} = 0.019$
$Y_{O_2} = 6 \times 10^{-4}$	$Y_{(WO_3)_{n=1-3}} = 1\text{–}3.5 \times 10^{-4}$	$Y_{O_2} = 3.6 \times 10^{-4}$	$Y_{(WO_3)_{n=1-3}} = 1\text{–}4.2 \times 10^{-4}$

Further understanding of coupling and competitive reaction mechanisms will be needed in the near future to develop accurate models and mechanisms for the chemical erosion of rocket nozzles.

Assuming local thermodynamic equilibrium due to fast, high-temperature kinetics, estimates are made of the species present within the boundary layer of the tungsten nozzle. This is done by assuming a large portion of an equilibrium mixture to be crystallographic tungsten, as illustrated by the large quantity remaining in the equilibrium mixture (Table 3). The certainties of these results are limited not only by the accuracy of available thermodynamic data, but also by the number of known and characterized species available. The thermodynamic database used was the standard package provided with CEA, with several additional species and data included: namely, solid and gas phases of tungstic acid [$WO_2(OH)_2$] [37] and tungsten hexacarbonyl [$W(CO)_6$] [38], as well as solid phase ditungsten carbide (W_2C) [38]. The calculations indicated $WO_2(OH)_2$ and WO_2Cl_2 as the primary tungsten containing products. Tungsten trioxide (WO_3) and its polymers are predicted to occur in greater quantities than WO_2. Assuming that in a simple W–O_2 (or W–CO_2) system the primary species formed is $(WO_3)_n$, this result provides a simple explanation and prediction of high-temperature tungsten oxidation rates while complicating overall mechanisms. The addition of Cl_2 in the presence of O_2 increases the stoichiometric coefficient (i.e., W/O ratio) by forming the WO_2Cl_2, in turn increasing the tungsten oxidation or corrosion rate. Applying this methodology to the addition of hydrogen into an O_2 system, forming $WO_2(OH)_2$ (i.e., reducing the stoichiometric coefficient), it is expected that oxidation rates would be reduced. Because chlorine and hydrogen are not present in the reaction systems of this study, WO_3 or its dimer or trimer is assumed to be the primary product species when O_2 and CO_2 are the only oxidizing species. Although tungsten dioxide (WO_2) is not a dominant equilibrium species, it may be a significant percentage of desorbed tungsten oxide, as indicated by the mass-spectrometric studies referenced.

IV. Conclusions

The heterogeneous reaction rates of bulk tungsten have been studied in the presence of oxygen, carbon dioxide, and carbon monoxide at high temperatures. Oxygen is a more efficient oxidizer with faster kinetics than CO_2, although both are found to oxidize tungsten at high rates, forming volatile oxide species and creating a linear mass loss of the bulk material at constant pressure and temperature conditions. The W–O_2 and W–CO_2 oxidation systems may be described using a single Arrhenius rate expression over the range of temperatures and pressures considered. The activation energy of the CO_2 reaction is nearly 3 times larger than the O_2 reaction (64 kcal/mol vs 23.5 kcal/mol). Computational and simplified theories indicate that the least energetically favorable reactions are surface oxide combination or desorption reactions. The pressure exponent of the CO_2 reaction is found to be 0.6 versus 0.89 for the O_2 reaction. Carbon monoxide does not oxidize tungsten to a volatile oxide; however, when added to a constant CO_2 concentration mixture the overall oxidation rates are reduced significantly, providing further evidence of the importance in understanding detailed heterogeneous reaction mechanisms of single-, as well as multicomponent systems in order to model nozzle erosion rates. Simplified analysis of the reaction kinetics of CO_2, CO, and O_2 indicates that nozzle recession rates may be appreciably affected through small manipulations of propellant formulations without sacrificing propellant performance. This implies that rocket motor performance may be affected by small perturbations in propellant formulation due to changes in nozzle erosion rates.

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