Rhenium/Oxygen Interactions at Elevated Temperatures

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Abstract

The oxidation of pure rhenium is examined from 600-1400°C in oxygen/argon mixtures. Linear weight loss kinetics are observed. Gas pressures, flow rates, and temperatures are methodically varied to determine the rate controlling steps. The reaction at 600 and 800°C appears to be controlled by a chemical reaction step at the surface; whereas the higher temperature reactions appear to be controlled by gas phase diffusion of oxygen to the rhenium surface. Attack of the rhenium appears to be along grain boundaries and crystallographic planes.

Introduction

Rhenium and its alloys have long been favored materials for small rocket engines, which move satellites into orbit. Rhenium has a very high melting point (>3180°C), thermally cycles well, and is stable in reducing atmospheres. However, like many refractory metals, it readily reacts with oxygen and forms a series of thermodynamically stable volatile rhenium oxides.

The thermodynamics of rhenium oxides have been studied by several investigators (1-4). At the temperatures of interest here the oxides are all gaseous. There are three principle oxides: $Re_2O_7(g)$, $ReO_3(g)$, and $Re_2O_6(g)$. Thus, the principal reactions are:

$$2\ Re(s) + 7/2\ O_2(g) = Re_2O_7(g) \tag{1a}$$

$$Re(s) + 3/2\ O_2(g) = ReO_3(g) \tag{1b}$$

$$2\ Re(s) + 3\ O_2(g) = Re_2O_6(g) \tag{1c}$$
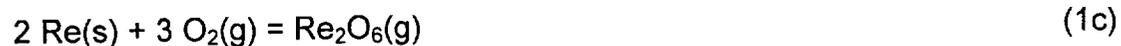
The first oxide has been extensively studied, less is known about the second, and relatively little about the third.

There are a several studies in the literature on the kinetics of Re-oxygen interactions. Lavrenko (5) has studied the oxidation of Re from 350-750°C, finding linear reaction rates. Gulbransen et al (6) have examined the oxidation of Re in flowing oxygen from 600-1400°C in oxygen from 1-10 torr. At the lower temperatures the process was controlled by a chemical reaction at the interface; at higher temperatures the process was controlled by gas phase diffusion to the sample. More recently, Alnot and Ehrhardt (7) have examined the oxidation of Re at 427°C and 1 torr of oxygen with X-ray Photoelectron Spectroscopy (XPS) and Ultra-Violet Photoelectron Spectroscopy (UPS). They found ReO_2, ReO_3, and Re_2O_7 on the Re surface.

In this study, we examine the interaction of rhenium with oxygen at temperatures from 600-1400°C in O_2/Ar mixtures. Flow rates, gas pressures, and temperatures were methodically varied in order to determine the rate controlling steps. In addition, the microstructures after reaction were examined.

Experimental

Rhenium as a rolled sheet was cut to coupons measuring 1 x 1 x 0.1 cm. The only impurities in this material were iron at 152 ppm and titanium at 16 ppm. Figure 1 is an micrograph of the material before reaction, illustrating some limited porosity, surface cracks, and a grain size of ~1 μm.

A series of oxygen/argon gas mixtures were prepared. The samples were suspended in a furnace tube connected to sensitive recording microbalance as a standard thermogravimetric apparatus (TGA). Temperature was varied from 600-1400°C. At all temperature a flow rate of 100 cc/min (STP) and an 300 ppm oxygen/argon mixture was used. At 600 and 1000°C flow rates were varied from 100-400 cc/min (STP). Also at 1000°C 10, 300 and 4000 ppm oxygen/argon mixtures were used. Two to three runs were done per condition. The duration of the run was generally 24 hrs; however, at the higher temperatures a reliable linear rate constant was attained in ~5 hrs.

After the oxidation runs, selected samples were examined with conventional scanning electron microscopy (SEM) using a JEOL 6100 microscope. Some X-ray diffraction (XRD) work was done to determine if any oxide remained on the surface.

Results and Discussion

Figures 2(a) and (b) show typical weight loss curves at 1200 and 600°C and 100 cc/min. At higher temperatures, the kinetics were smoothly linear with no clear induction period. At lower temperatures, there appear to be two linear regions. The first region was brief and thus rate constants were extracted from the second region for analysis.

These linear rates are characteristic of gas/solid reactions which produce volatile reaction products. There are three possibilities for rate-controlling steps:

1. Diffusion of the reactant gas (oxygen in this case) through the static boundary layer to the solid sample surface.
2. The chemical reaction at the gas/solid interface.
3. Diffusion of the product gases ($Re_2O_7(g)$, $ReO_3(g)$, and/or $Re_2O_6(g)$ in this case) through the static boundary layer, away from the solid sample surface.

Reaction rate dependence on flow rates and partial pressure of oxygen are useful tools to discriminate amount these possibilities. Gas-phase diffusion-limited processes show a gas flow rate to the half-power dependence (8). The free energy of formation of the Re-oxides is strongly negative relative to the metal. This fact suggests that if a gas-phase diffusion-limited process is rate controlling, it is supply of oxygen to the sample—step 1 in the above list.

Figure 3(a) and 3(b) are plots of log(reaction rate) vs log(gas velocity) 1000 and 600°C, respectively. At 1000°C, there is a clear variation of reaction rate with flow rate to the 0.65 power. At 600°C, reaction rate seems nearly independent of flow rate. The pressure dependence at 1000°C is shown in Figure 4. There is a clear linear pressure dependence over the range of interest. Thus both the velocity and the pressure dependence indicate that oxygen inward is rate controlling at 1000°C.

The observed reaction rates (k) can be estimated from the well-established correlation for a flat plate (9):

$$k = 0.664 \, (Re)^{0.5} \, (Sc)^{0.33} \, p(O_2) \frac{D}{L}$$

$$Re = \frac{\rho \, v \, L}{\eta} \qquad\qquad\qquad (2)$$

$$Sc = \frac{\eta}{\rho \, D}$$

Here Re and Sc are the Reynolds and Schmidt numbers, respectively. In these expressions, ρ is the density of the O_2-Ar mixture, $\rho\,(O_2)$ is the density of the O_2 reactant, v is the linear gas velocity, η is the viscosity taken as 6.16×10^{-4} poise, L is a characteristic dimension taken as 0.5 cm, and D is the diffusivity of either the O_2 reactant. The latter is estimated from the Chapman-Enskog correlation (9):

$$D = \frac{0.001858\,T^{3/2}}{P\,(\sigma_{Ar-O_2})\,\Omega_{Ar-O_2}} \left(\frac{1}{M_{Ar}} + \frac{1}{M_{O_2}}\right)^{1/2} \tag{3}$$

Here T is the absolute temperature, P is the total pressure, (σ_{Ar-O_2}) is the average collision diameter, which is average of the molecular diameters of Ar and O_2, Ω_{Ar-O_2} is the collision integral, available in tabulations.

Note that the rate constant calculated in equation (2) is only the flux of oxygen reaching the surface. According to a free energy minimization calculation (4), the principle reaction for the oxidation of Re is 1(a). Thus the flux from expression (2) must be multiplied by 3.32 for comparison to the linear reaction rate measured as total weight loss.

The calculated reaction rates along with the measured rates are shown in Figure 5. Note that the weak temperature dependence of gas-phase diffusion limited rates. Agreement of the calculated and measured rates is reasonable at 1000, 1200 and 1400°C, further supporting gas-phase diffusion limited rates. However, at 600 and 800°C, the measured rates are much lower that those predicted from gas-phase diffusion. This suggests another mechanism.

Figure 3(b) illustrates the flow rate dependence of reaction rate at 600°C. The near zero slope of the line indicates no flow rate dependence. Thus transport of oxygen inward through the static boundary layer cannot be rate controlling.

However the reaction rates are still linear, as illustrated in Figure 2(b). Thus the chemical reaction at the surface is very likely rate controlling. The two reaction stages in Figure 2(b) are possibly caused by preferential attack of different microstructural features. This behavior is also indicative of chemical reaction control.

Thus gas-phase transport of oxygen inward is rate controlling at 1000-1400°C whereas chemical reaction is likely rate-controlling at 600 and 800°C. This type of transition from chemical reaction control at lower temperatures to gas-transport control at higher temperatures is commonly observed in oxidative vaporization. Gulbransen et al. (5) have studied oxidation of Re in 1, 2, 5, and 10 torr oxygen total pressure from 600-1400°C. Below 1100°C, they observe chemical reaction control; above 1100°C they observe gas-phase diffusion control. For tungsten oxidation, Bartlett (10) found this transition from chemical reaction to gas-phase diffusion control 2000°C.

The morphology of attack at 800°C is illustrated in Figure 6. Note the contrast to Figure 1. There appears to be preferential attack along certain crystallographic planes and at the grain boundaries. At higher temperatures this attack was similar, but more pronounced.

Summary and Conclusions

The oxidation of Rhenium has been studied from 600-1200°C in dilute oxygen/argon mixtures. Linear oxidation rates were measured throughout this range. Flow rate and pressure dependence suggests that the gas phase diffusion of oxygen inward is rate controlling at 1000- 1400°C; whereas the chemical reaction of oxygen and Re is rate controlling at 600 and 800°C. Microstructures of oxidized Re indicate attack is primarily along grain boundaries and certain crystallographic planes.

Acknowledgements

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Figure Captions:

1. Micrograph of starting material, illustrating surface cracks, limited porosity, and grain boundaries (5000X).

2. Representative TGA curve of Re oxidation at (a) 600°C (b) 1000°C.

3. Plot of log(rate constant) vs log(velocity) to extraction exponential dependence of rate on velocity at: (a) 600°C (b) 1000°C.

4. Plot of rate constant vs pressure at 1000°C and 100 cc/min.

5. Plot of ln(rate constant) vs. inverse temperature for experimental results (solid line) and calculated results (dashed line).

6. Rhenium surface morphology after 24 hr oxidation at 800°C (5000X).

Fig 1

Re at 1000 °C
100 ccm (309 ppm
oxygen in argon)

(a)

Re at 600 °C
100 ccm (334 ppm
oxygen in argon)

(b)

Fig 2

Fig 3

Fig 4

Fig 5

Fig 6