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P. D. Ownby

Missouri University of Science and Technology, ownby@mst.edu

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## OXIDATION STATE CONTROL OF VOLATILE SPECIES IN SINTERING

P. Darrell Ownby

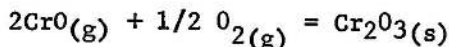
Ceramic Engineering Department  
University of Missouri-Rolla  
Rolla, Missouri 65401 U.S.A.

### INTRODUCTION

The hinderance to sintering created by oxidation state changes which produce volatile phases is well known. The chromium-oxygen system provides an excellent example to illustrate the problems associated with these types of phase changes. Chromium sesquioxide is an attractive refractory material with three other oxides in the system as well as chromium metal having a considerable vapor pressure. Attempts to sinter chromium sesquioxide powders must include provisions for the stabilization of this phase if sintering to high density is to be successful. <sup>(1)</sup>

Figure 1 shows the standard free energy of formation of three of the chromium oxides as a function of temperature. Scales on the right indicate the partial pressure of oxygen in equilibrium with the reactions shown as a function of temperature. The dotted lines show the values of the equilibrium oxygen pressures for the three oxides at 1600°C, the temperature selected for illustration. The outer two scales on the right show two means of achieving the adjacent oxygen pressures using buffer systems based on the equilibrium decomposition of H<sub>2</sub>O and CO<sub>2</sub>, respectively. H. H. Kellogg <sup>(2)</sup> has written an excellent review of the graphical relationships between the partial pressures of the vapor species in binary systems as a function of the non-metal partial pressure. Figure 2 was calculated for 1600°C following Kellogg, but not omitting CrO and CrO<sub>2</sub> as did Graham and Davis. <sup>(3)</sup> The slopes

of the lines are fixed by the mass action law and represent the equilibrium partial pressures of vapor species assuming unit activity of chromium and  $\text{Cr}_2\text{O}_3$  in their respective phase fields; i.e.



$$K = \frac{1}{(P_{\text{CrO}})^2 (P_{\text{O}_2})^{1/2}}$$

$$P_{\text{CrO}} = K^{-1/2} (P_{\text{O}_2})^{-1/4}$$

The  $P_{\text{CrO}}$  and  $P_{\text{CrO}_2}$  curves were fixed on the dotted vertical axis from interpolation of the mass spectrometric data of Grimley, et al. (4) to  $1600^\circ\text{C}$ . It was assumed that the equilibrium oxygen partial pressure was the sum of the  $P_{\text{O}_2} + 1/2 P_{\text{O}}$  detected by the mass spectrometer. An error in this assumption would not change the slopes and would only change the vertical position of these curves slightly. The total of these four partial pressures is dotted in the  $\text{Cr}_2\text{O}_3$  field.

The sintering of chromium sesquioxide has been found to be enhanced by neutral or reducing atmospheres. (5,6) Although the difficulty of sintering in oxidizing atmospheres has been attributed to the formation of the high vapor pressure  $\text{CrO}_3$ , a systematic study over a large range of oxygen partial pressures has been lacking.

At  $1600^\circ\text{C}$ , equilibrium reduction to metallic chromium does not occur at oxygen pressures above  $2 \times 10^{-12}$  atm ( $\log P_{\text{O}_2} = 10^{-11.7}$ ) as shown on Figures 1 and 2. To achieve known oxygen partial pressures in this low range requires a buffer system where the equilibrium decomposition of a gaseous oxide is used to fix the oxygen partial pressure. (7)

#### EXPERIMENTAL

Ultra high purity (99.99%) chromium sesquioxide produced by the oxidation of ultra high purity chromium was used to produce 1/2" diameter samples. The powder was examined by electron microscopy and found to consist of submicron particle agglomerates about 10 microns in diameter. The uniaxially formed discs were isostatically pressed to 30,000 psi to about 63% of the theoretical density.

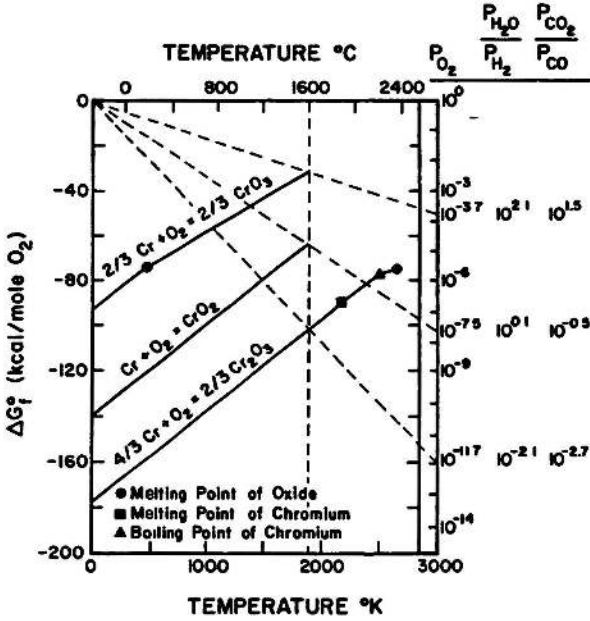


Figure 1. The Standard Free Energy of Formation of Chromium Oxides as a Function of Temperature.

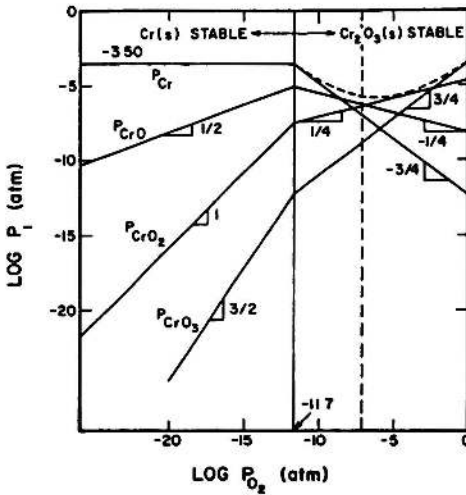


Figure 2. The Equilibrium Partial Pressures of the Vapor Species over Solid Chromium and Solid Chromium Sesquioxide as a Function of Oxygen Partial Pressure at 1600°C.

The specimens were sintered in high purity alumina boats in a molybdenum wound, controlled atmosphere, tube furnace at 1600°C for one hour.<sup>(8)</sup>

Initially, the H<sub>2</sub>O/H<sub>2</sub> buffer system was used to fix the oxygen partial pressure over the samples. The H<sub>2</sub>O/H<sub>2</sub> ratios were controlled by bubbling hydrogen through a distilled water, constant temperature bath.

The final experiments were made using the CO<sub>2</sub>/CO buffer system which was easier to control and provided a more accurate means to fix the oxygen partial pressure. The CO<sub>2</sub>/CO ratios were maintained by passing each gas through a calibrated flow meter and then through a glass-bead filled, pre-furnace, mixing chamber. To produce the lowest CO<sub>2</sub>/CO-ratios, a mixed gas of 5% CO<sub>2</sub> and 95% nitrogen was used.

For both buffer systems the total gas flow rate through the furnace tube was fixed at one linear centimeter per second to maintain equilibrium with the sample.<sup>(7)</sup>

#### RESULTS & DISCUSSION

Figure 3 shows the percent of theoretical density of chromium sesquioxide sintered at 1600°C for 1 hour as a function of oxygen partial pressure as maintained by the

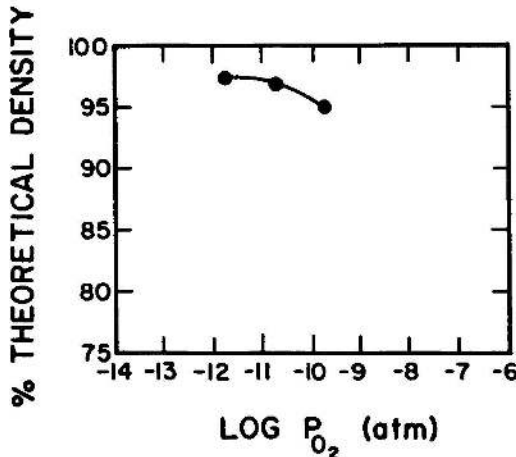


Figure 3. The Percent of Theoretical Density as a Function of Oxygen Partial Pressure of Chromium Sesquioxide Sintered at 1600°C for One Hour Using the H<sub>2</sub>O/H<sub>2</sub> Buffer System.

H<sub>2</sub>O/H<sub>2</sub> buffer system. The density increased to >97% as the oxygen pressure was reduced approaching the minimum value for stability of the sesquioxide.

The control with this system was not satisfactory, nor was the degree of accuracy in determining the H<sub>2</sub>O/H<sub>2</sub> ratio. The high densities achieved by this technique, did however, provide the impetus for more carefully examining the density dependence over a wide range of oxygen pressures.

Figure 4 shows the density dependence at 1600°C for 1 hour over the entire range of oxygen pressures from 1 atm to 10<sup>-13</sup> atm. The highest oxygen pressure points were obtained using oxygen, air, and commercial nitrogen in order of decreasing pressure. A pronounced increase in density is observed as the equilibrium oxygen pressure between the two phases, chromium metal and chromium sesquioxide, is approached. The maximum density, 99.4%, was found at that equilibrium pressure (see Figures 1 and 2).

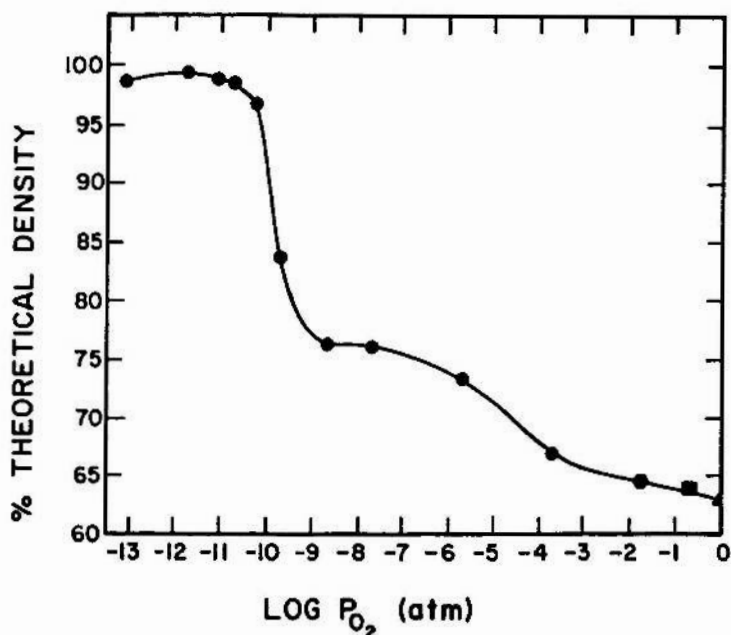


Figure 4. The Percent of Theoretical Density as a Function of Oxygen Partial Pressure of Chromium Sesquioxide Sintered at 1600°C for One Hour Using the CO<sub>2</sub>/CO Buffer System to Control the Oxygen Pressure.

In other sintering studies on  $\text{Cr}_2\text{O}_3$  the oxygen partial pressure has either been unknown or too high.<sup>(6,9,10)</sup> In the initial sintering experiments of Hagel, et al.<sup>(6)</sup>, the oxygen partial pressure was unknown (although they reported a  $P_{\text{O}_2} \approx 1.3 \times 10^{-5}$  atm) because of the graphite specimen holders used. In repeating the above experiments, without graphite boats, Anderson's pressure was known<sup>(9)</sup> ( $\approx 10^{-5}$  atm) but he could not reproduce their data. This might be expected from the data in Figure 4, since Hagel's oxygen pressure was probably much lower, i.e. in the  $10^{-10}$  to  $10^{-13}$  range, where sintering would be enhanced, whereas not much sintering would be expected at  $10^{-5}$ . Other workers, such as Stone,<sup>(10)</sup> have added powder reductants such as carbon to promote sintering with some success, however, in these experiments the actual oxygen pressure achieved remains unknown.

Figure 5 shows the experimental and calculated weight loss dependence on oxygen pressure at  $1600^\circ\text{C}$  for one hour. The calculated curve was determined by adding the product of the vapor pressure from Figure 2 and the molecular weight of each species. Percent weight losses were computed by fixing the value of this sum at 1 atm oxygen pressure to the experimental value of 2.1%. This calculation agrees quite well with the experimental values. The small weight loss in the middle of the range where almost none is predicted could be due to moisture or loss of other adsorbed species.

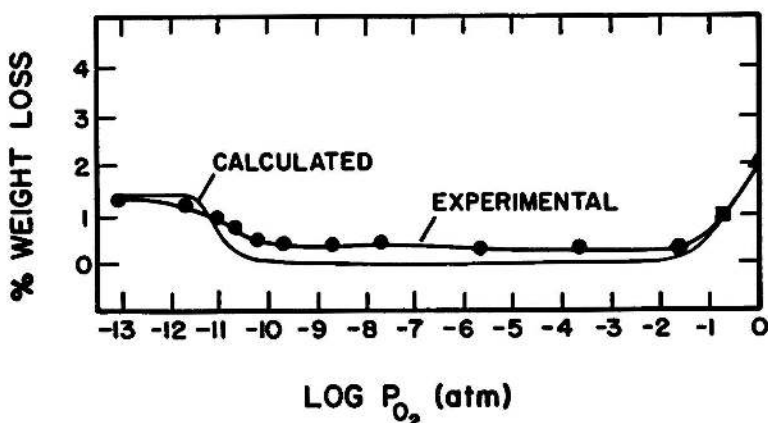


Figure 5. The Percent Weight Loss of Chromium Sesquioxide as a Function of Oxygen Partial Pressure at  $1600^\circ\text{C}$  for One Hour.

## CONCLUSIONS

Oxidation state control can be very important in sintering studies where many possible states involving volatile species exist. An analysis of the non-metal vapor pressure dependence of these volatile species can provide a useful tool in predicting such important phenomena as densification and weight loss.

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