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ABSTRACT

Target collection techniques and high pressure mass spectrometric sampling have been used to study the formation of volatile chromium-containing species in the reaction of $Cr_2O_3(c)$ with $O_2(g)$ and NaCl(g). Experiments were performed at atmospheric pressure as a function of chromium temperature, oxygen pressure, and NaCl(g) concentration. The major chromium-containing vapor species were found to be $(NaCl)_xCrO_3(g)$, with $x = 1,2$, and 3, which are products of heterogeneous reactions on the surface. The kinetics indicate first order dependence on oxygen and sodium chloride pressures.

INTRODUCTION

Equilibrium thermodynamic calculations indicate that for gas turbine engines operating under conditions favoring hot corrosion attack, the engine hot-section environment should be rich in the contaminant gases NaCl(g),* NaOH(g), and HCl(g) (Ref. 1). These highly reactive chemical species are expected to play a significant role in the hot corrosion process and indeed it has been shown (Ref. 2-4) that NaCl(g) can compromise the so-called protective oxide scale on certain superalloys used in turbine engines. The phenomenology of interaction between oxidized metal and the gaseous species NaCl(g), NaOH(g), and HCl(g) is not well characterized and the operative mechanisms are not understood. To elucidate the kinetics and mechanisms of such interactions, we have been studying various metal oxide-oxygen-contaminant gas systems. The work reported here is for the initial phases of our investigation of the $Cr_2O_3(c)$ - $O_2(g)$ - NaCl(g) system.

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*Throughout this paper, (c) refers to condensed state and (g) refers to gas.

EXPERIMENTAL

Two experimental techniques have been employed in the present study. These techniques are target colletion and high pressure sampling mass spectrometric analysis. Schematic representations of the apparatus used for each technique are shown in Figure 1. From the figures, it can be seen that part of the apparatus is common to both techniques. A sample of pure chromium, measuring approximately 1 x 1 x 0.3 cm, is suspended by a platinum wire inside a 2.5 cm diameter quartz tube in a 15 cm long tube furnace. The furnace is controlled through a thermocouple by a precision set-point controller coupled to a saturable core reactor power source. The sample is heated in a low velocity (6 cm/sec) stream of flowing gas. All experiments were performed at atmospheric pressure. Oxygen partial pressures were varied by diluting the oxygen flow with argon. Partial pressures of NaCl(g) were developed by heating a platinum crucible containing NaCl(c). The crucible, which measured 2 cm long by 0.8 cm diameter, is mounted on a 3 mm diameter quartz tube containing a double bore alumina thermocouple tube. The crucible assembly is inside a 1.3 cm diameter inner quartz tube inside the 2.5 cm outer quartz tube. The inner tube extends to about one centimeter below the sample. The inner and outer tubes are independently fed from a common gas supply and the flow is adjusted to give a gas velocity through the inner tube approximately double that through the outer tube. Total gas flow through the apparatus was 500 cc/min. The crucible assembly can be moved vertically through a slip seal and the crucible temperature is varied by changing its position vertically in the furnace. The crucible temperature is continuously measured with a Pt-Pt 13% Rh thermocouple extending up into the crucible base. The temperature of the chromium sample was measured with a similar thermocouple contacting the side of the sample.

In all experiments, the chromium sample was allowed to oxidize for several hours before being exposed to reduced oxygen pressure or NaCl(g). In the target collection experiments, volatile products emanating from the quartz tube were collected on 5 x 5 x 0.04 cm platinum targets mounted on a water cooled copper plate positioned about 2 cm above the mouth of the quartz tube. As shown in Figure 1a, a platinum collimator, with a 2 cm diameter opening, was located between the collection target and quartz tube. Deposits collected on the targets, as a function of time, were completely dissolved from the targets with water. The resulting solutions were analyzed for chromium and sodium by atomic absorption spectroscopy, and for chlorine by a colorimetric method.

For identification of gaseous species emanating from the system under study, the high pressure mass spectrometric sampling apparatus shown (very schematically) in Figure 1b was used. The 0.02 cm diameter sampling orifice is mounted on the end of a 1.2 cm long by 1.8 cm diameter stainless steel tube. The sampling orifice protruded into the quartz tube about 1 cm and was thus allowed to reach a temperature approaching that of the chromium sample. Heating of the orifice was found to be necessary to prevent condensation and subsequent clogging of the orifice.

The free-jet expansion, four-stage sampler facilitates sampling at atmospheric pressure and preserves the integrity of sampled species which are formed into a molecular beam for mass analysis by the quadrupole mass spectrometer. The skimmed molecular beam is modulated by a slotted rotating disk located in stage 2 behind the skimmer. The theory and details of the free-jet expansion sampling technique are given in the literature (Ref. 5-8).

RESULTS AND DISCUSSION

Target Collection Experiments. Chromium samples heated in the temperature range from 850 to 1050°C, in pure oxygen, developed a compact scale of $Cr_2O_3(c)$. For all experiments, the chromium sample was allowed to develop the oxide coating for at least two hours prior to any further experiments. No spalling was observed at temperature in the course of the experiments and the sample was considered to be $Cr_2O_3(c)$.

When oxygen alone was flowed over the hot oxidized chromium, a yellow-brown deposit was collected on the platinum target. Based on previous studies (Ref. 9), this deposit was presumed to be $CrO_3(c)$, the condensed product of the oxidative vaporization reaction:

$$\frac{1}{2}\,Cr_2O_3(c) + 3/4\ O_2(g) = CrO_3(g) \qquad (1)$$

The rate of chromium collection (r_{Cr} in ug/hr, in this case) was found to be independent of time.

The rate, r_{Cr}, was measured as a function of the chromium sample temperature, T_{Cr}, and found to obey the relationship shown in the Arrhenius plot in Figure 2. The circled points are experimental data and the line is a least squares fit of the data. Because these data were obtained primarily to serve as a baseline for other parts of this study, no attempt was made to extract thermodynamic results by applying geometrical, diffusion-limitation, or gas temperature corrections to the data.

When partial pressures of NaCl(g) were added to the oxygen flow, the rate of chromium collection increased significantly. The collected deposit was still yellowish in color and readily water soluble. The deposit was presumed to contain NaCl(c), $CrO_3(c)$, and some other chromium-containing compounds. Because an enhancement was observed when NaCl(g) was present, we considered the oxidative vaporization reaction, equation (1), to be taking place simultaneously with other reactions. Therefore the rate of chromium collection from the other reactions, R_{Cr}, was considered to be the difference between the total rate, ${}_TR_{Cr}$, and the rate for oxygen alone, r_{Cr}, i.e.;

$$R_{Cr} = {}_TR_{Cr} - r_{Cr} \tag{2}$$

The value of R_{Cr} was found to be a function of the concentration of NaCl(g), oxygen pressure, and chromium sample temperature. For convenience, we have chosen to express the sodium chloride concentration as an effective pressure P_{NaCl} in torr. P_{NaCl} was calculated from vapor pressure data (Ref. 10) by taking into account that NaCl(c) vaporizes mainly as both the monomer and dimer. The equation used is

$$P_{NaCl} = 2\ p_{Na_2Cl_2} + p_{NaCl} \tag{3}$$

where $p_{Na_2Cl_2}$ and p_{NaCl} are the vapor pressures of the dimer and monomer respectively. (The trimer and higher polymers of NaCl(g), which are present in low concentrations in the equilibrium vapor over NaCl (Ref. 11), were ignored.) P_{NaCl} is <u>not</u> the absolute partial pressure of sodium chloride gas in the apparatus; P_{NaCl} is merely proportional to the concentration of sodium chloride gas. When the platinum crucible containing the NaCl(c) was at 826°C (the highest temperature used in our experiments), P_{NaCl} was calculated to be 0.85 torr. We have estimated from target collection data taken under these condtions that the actual concentration of sodium chloride gas is approximately 27 ppm which is about a factor of 40 less than the saturated equilibrium value.

The variation of R_{Cr} with P_{NaCl}, at a constant chromium sample temperature of 1020°C and one atmosphere oxygen pressure, is shown in Figure 3. The range of P_{NaCl} shown in this figure is for platinum crucible temperatures in the range from 550 to 826°C. Two points must be emphasized with regard to the results given in Figure 3: (1) in all cases, the salt temperature was sufficiently below that of the chromium sample to assure that no condensation of NaCl occurred on the sample and (2) the fact that an increased rate was obtained in the presence of NaCl(g) indicates that the rate is not limited by the vaporization rate of $CrO_3(g)$; i.e., the increased rate of chromium deposition is not the result of gas phase reactions.

The functional dependence of R_{Cr} on chromium sample temperature is presented in Figure 4 for constant values of P_{NaCl} and P_{O_2}. In Figure 5, the variation of ${}_{T}R_{Cr}$ with oxygen pressure is shown for constant values of T_{Cr} and P_{NaCl}. Here the total chromium rate is plotted because one cannot merely substract r_{Cr} for the CrO_3 since r_{Cr} also is a function of oxygen pressure (Ref. 9). The partial pressures of oxygen were obtained experimentally by diluting the oxygen flow with argon. Uncalibrated rotometers were used and this probably accounts for the scatter in the data. The results are however sufficiently accurate to indicate that ${}_{T}R_{Cr}$ is linearly dependent on P_{O_2}.

<u>High Pressure Sampling Mass Spectrometer Experiments</u>. Attempts to mass spectrometrically identify the vaporizing species $CrO_3(g)$, in the case where only oxygen was flowed over the oxidized chromium sample, have been unsuccessful. In this case, no vapor species emanating from the apparatus have been detected, except of course oxygen. At the highest temperatures available with the present apparatus the concentration of the $CrO_3(g)$ species was estimated from target collection data to be about 0.03 ppm, which appears to be just below the detection sensitivity of our sampling system.

For the case where NaCl(g) is added to the oxygen flowing over the oxidized chromium, numerous vapor species emanating from the apparatus have been detected. Tests were performed with a chromium sample temperature of 1020°C, an oxygen pressure of one atmosphere and sodium chloride concentrations in the range P_{NaCl} = .4 to 1.0 torr. The ions observed, their relative intensities, and the probable parent molecular species vaporizing are presented in Table I. In addition to the ions containing sodium and chlorine, a number containing chromium have also been observed. The vaporizing chromium-containing species are seen to be mainly complexes of

NaCl and CrO_3. Many complex molecules containing only metal and halogen atoms have been reported previously (Ref. 11-13). We believe that the $(NaCl)_xCrO_3$ ($x = 1,2$, or 3) molecules reported herein are the first observed examples of alkali halide-metal oxide type vapor complexes. The only species containing just Na, Cr, and O observed is $Na_2Cr_2O_7$ and this is a relatively minor constituent of the vapor. Again it must be emphasized that the identified species are not likely the product of gas phase reactions because if they were, the rate controlling step would be the volatilization of CrO_3 and there would be no enhancement in rate with NaCl(g) added. Each species reported in Table I was found to vanish when the NaCl(g) was removed.

It has been suggested by several investigators (Refs. 4(a), 14-17) that when NaCl(g) reacts with Cr_2O_3(c) scales, volatile chromium compounds are formed with sodium chromate remaining on the surface. The volatile compounds suggested were CrO_2Cl_2, $CrCl_2$, and $CrCl_3$ (Refs. 4, 14, 16-19). Other investigators speculate that sodium chromate may be formed and vaporized (Refs. 14, 15). In our investigation, we have made an exhaustive search for the species CrO_2Cl_2(g), $CrCl_2$(g), $CrCl_3$(g), and Na_2CrO_4(g) but these were not detected. We have made Knudsen cell studies of the vaporization of Na_2CrO_4(c) in vacuum and established that this compound vaporizes with the species Na_2CrO_4(g) being at least 50% of the vapor product. We have also with the present apparatus put Na_2CrO_4(c) in the platinum crucible in place of NaCl(c) (with the chromium sample removed from the apparatus) and readily detected Na_2CrO_4(g). Based on our findings in the present study, we are led to conclude that sodium chromate is not formed in the reaction between Cr_2O_3(c), O_2(g), and NaCl(g). The main reaction responsible for the transport of chromium is

$$Cr_2O_3(c) + 3/2\ O_2(g) + xNaCl(g) = (NaCl)_xCrO_3(g) + CrO_3(g) \quad (4)$$

where $x = 1,2$, and 3.

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TABLE I

MASS SPECTRUM OF VAPORS OVER THE $Cr_2O_3(c)$ - $O_2(g)$ - $NaCl(g)$ SYSTEM. EXPERIMENTAL CONDITIONS ARE GIVEN IN THE TEXT.

Ion[a]	Relative Intensity[b]	Probable Parent Molecule[c]
Na^+	0.8	$NaCl$
O_2^+	1.62×10^4	O_2
$NaCl^+$	1.00	$NaCl$
Na_2Cl^+	0.57	$(NaCl)_2$
$NaCrO_3^+$	2.2×10^{-2}	$NaClCrO_3$
$Na_3Cl_2^+$	6.0×10^{-2}	$(NaCl)_3$
$NaClCrO_3^+$	2.5×10^{-2}	$NaClCrO_3$
$Na_2ClCrO_3^+$	4.8×10^{-2}	$(NaCl)_2CrO_3$
$Na_4Cl_3^+$	1.0×10^{-3}	$(NaCl)_4$
$Na_3Cl_2CrO_3^+$	2.0×10^{-3}	$(NaCl)_3CrO_3$
$Na_2Cr_2O_7^+$	4.0×10^{-3}	$Na_2Cr_2O_7$
$Na_3Cr_2O_7^+$	1.0×10^{-3}	$NaClNa_2Cr_2O_7$

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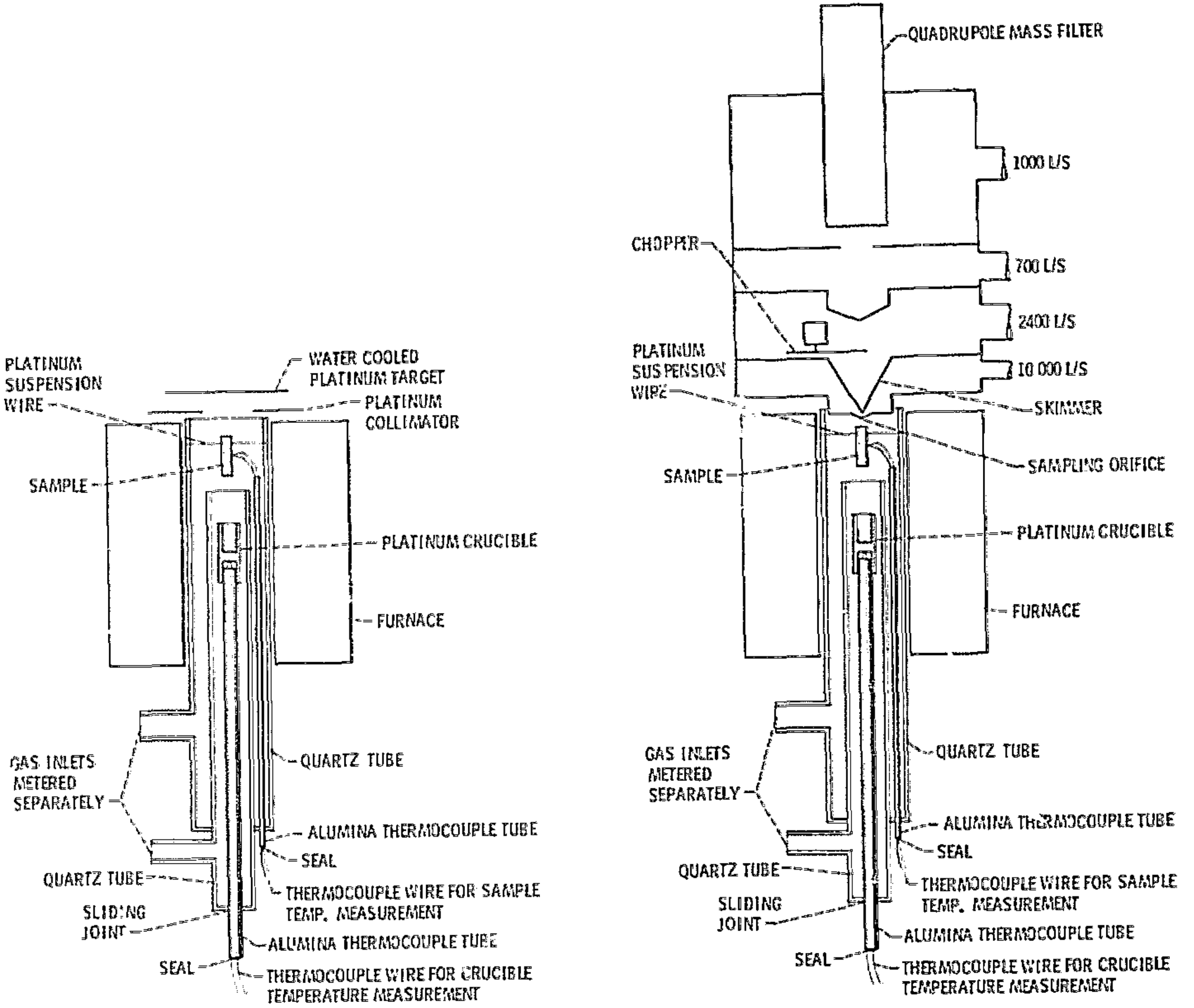
[a] In all cases, ions were identified by their m/e values, isotopic abundance distribution, and behavior when either $NaCl(g)$ or $Cr_2O_3(c)$ was removed from the system.

[b] Relative ion intensities can be converted to correct ratios of partial pressures only if reliable values are available for the relative ionization and fragmentation cross sections, multiplier gains, quadrupole mass filter transmission, and Mach-number focusing factors for each species. At present, most of these quantities are unknown for the complex molecular species.

[c] Parent molecular species were assigned on the basis of the familiarity with the mass spectrum-molecular composition relatioship for other inorganic halide molecule systems. It is well established (Ref. 11) that halogen-containing molecules fragment upon electron impact ionization to yield molecular ions with the loss of a halogen atom; i.e.,

$$Na_2Cl_2(g) + e^- \rightarrow Na_2Cl^+ + Cl + 2e^-$$



(a) Schematic of target collection apparatus.

(b) Schematic of apparatus with high pressure mass spectrometric sampler.

Figure 1.

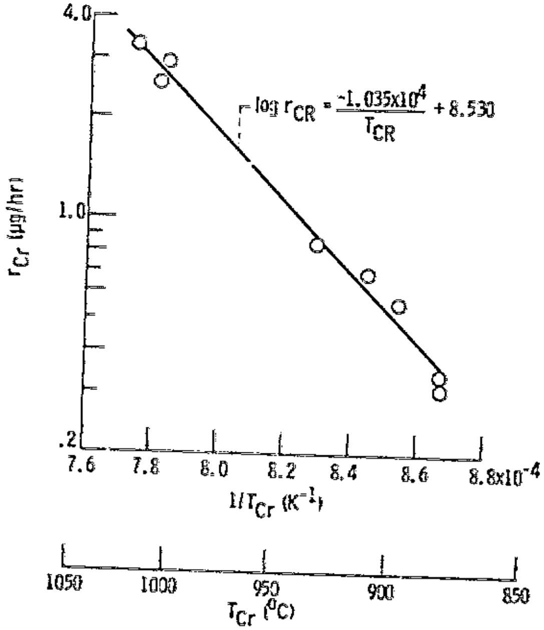


Figure 2. - Variation of CrO_3 (g) vaporization rate, r_{Cr}, with temperature of chromium sample, T_{Cr}, for the reaction $1/2\ Cr_2O_3(c) + 3/4\ O_2(g) = CrO_3(g)$.

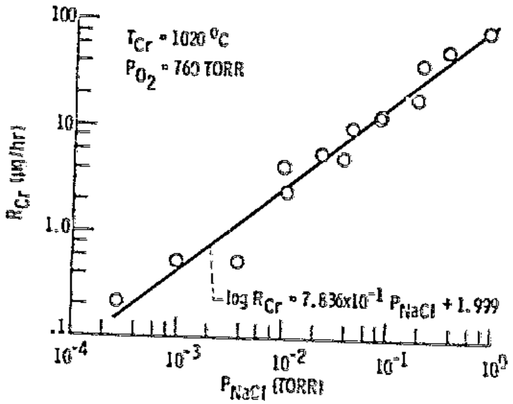


Figure 3. - Dependence of chromium collection rate corrected for CrO_3(g) vaporization, R_{Cr}, on effective sodium chloride pressure, P_{NaCl} at constant pressure of oxygen and chromium temperature.

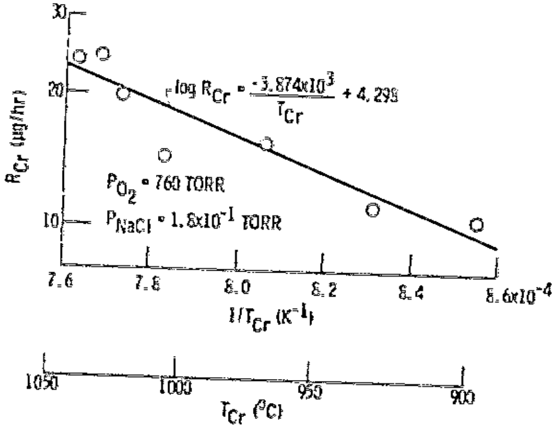


Figure 4. - Dependence of chromium collection rate corrected for CrO_3(g) vaporization, R_{Cr}, on chromium sample temperature, T_{Cr}, at constant pressures of oxygen and sodium chloride.

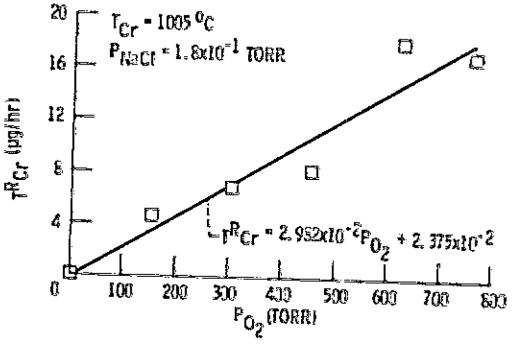


Figure 5. - Variation of total chromium collection rate, $_TR_{Cr}$, with oxygen pressure, P_{O_2}, at constant chromium sample temperature and sodium chloride pressure.