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VOLATILE PRODUCTS IN THE CORROSION OF Cr, Mo, Ti AND FOUR SUPERALLOYS EXPOSED TO O_2 CONTAINING H_2O AND GASEOUS NaCl

by George C. Fryburg, Robert A. Miller, Fred J. Kohl, and
Carl A. Stearns
Lewis Research Center
Cleveland, Ohio 44135

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Fred J. Kohl, and Carl A. Stearns

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

ABSTRACT

Cooled target collection techniques were used to study the formation of volatile products when samples of Cr, Ti, IN-738, 713C, NASA-TRW VIA and B-1900 were exposed, at elevated temperatures, to oxidizing environments containing $H_2O(g)$ and NaCl(g). Samples were heated to 1050° C in one atmosphere of slowly flowing oxygen, saturated with water at 21° C, and containing about 50 ppm NaCl(g). Volatile products were detected for all materials except B-1900 and Ti. High pressure mass spectrometric sampling was used to directly identify volatile products emanating from samples of Cr and IN-738 subject to the above environments. Mo samples were also studied at 675° C with 4 ppm NaCl(g) added to the O_2 + H_2O environment. For Cr and IN-738 the volatile species were identified primarily as $(NaCl)_{1,2,3}CrO_3$, $(NaOH)_{1,2}CrO_3$, $Na_2Cr_2O_7$ and $CrO_2(OH)_2$. These same species are deduced to prevail for 713C and NASA-TRW VIA. For Mo, the major species identified were $(NaCl)_{1,2}(MoO_3)_3$, $NaOH(MoO_3)_3$, $(MoO_3)_{3,4}$ and $MoO_2(OH)_2$.

[*]NRC Resident Research Associate

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INTRODUCTION

Equilibrium thermodynamic calculations applied to gas turbine engines operating under conditions thought to be conducive to hot corrosion attack indicate that the engine hot section environment should be rich in the contaminant gases NaCl(g), NaOH(g), and HCl(g) (Ref. 1). These chemical species are generally considered as highly reactive and therefore it seems reasonable to expect that they might play a significant role in the hot corrosion process. Previously it had been demonstrated that adverse effects could be associated with exposure of hot oxidizing metals to partial pressures of NaCl(g) (Refs. 2, 3, 4). Hancock et al. (Ref. 2) have shown that additions of NaCl(g) to the oxidizing environment can compromise the so-called protective oxide scale on certain alloys used in turbine engines. For the oxidation of chromium, Stearns et al. (Ref. 3) presented evidence which indicates that additions of NaCl(g) lead to increased rates of chromium transport from the sample. The results indicate first order dependence of Cr-compound vaporization on NaCl(g) partial pressures, and the vapor species were identified by high pressure mass spectrometry. Jones et al. (Ref. 4) recently have presented evidence to show that NaCl(g) can: (1) induce dissociation of $Na_2SO_4(c)$; (2) promote spalling of Al_2O_3 surface oxide; (3) remove Cr from samples as a volatile "chromchloride"; and, (4) accelerate the degradation, by sulfidative oxidation, of certain CoCrAlY coated alloys.

The phenomenology of interaction between oxidizing metals 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 investigating various metal-oxygen-contaminant gas systems at elevated temperatures. Our previously reported studies of $Cr + O_2 + NaCl(g)$ yielded some kinetic information for this system and identified $(NaCl)_{1,2,3}CrO_3(g)$ as the major volatilizing species (Ref. 3). The work reported here is a continuation of this effort and describes (1) the effect of adding water vapor to the $Cr + O_2 + NaCl(g)$ system, and (2) interactions of NaCl(g) and/or $H_2O(g)$ with Mo, Ti, and the superalloys NASA-TRW VIA, B-1900, IN-738 and 713C.

EXPERIMENTAL

Two experimental techniques were used in the present atmospheric pressure investigations; cooled target collection and high pressure mass spectrometric sampling. Schematics of the respective apparatus are shown in Figure 1. It can be seen that the furnace assembly apparatus was common to both techniques. The metal sample, measuring approximately $1 \times 1 \times 0.25$ cm, was suspended on a platinum wire within a 2.2 cm inside diameter quartz tube that was mounted in a 15 cm long tube furnace. The furnace temperature was controlled through a thermocouple by a precision set-point current proportionating controller coupled to a saturable core reactor power source. Temperatures could be maintained to $\pm 2^{\circ}$ C. Sample temperature was measured independently with a Pt-Pt 13 % Rh thermocouple inside the quartz tube and contacting the side of the sample.

Partial pressures of NaCl(g) were developed by heating NaCl(c) in a platinum crucible that was situated below the sample in a 1.3 cm diameter quartz tube. The crucible was 2 cm long by 0.6 cm in diameter and it was supported on a double bore alumina thermocouple tube. A Pt-Pt 13 % Rh thermocouple in the alumina tube extended into the crucible base and facilitated continuous measurement of the crucible temperature. A slip-seal system allowed the crucible assembly to be moved vertically so that the crucible temperature could be varied by changing its position in the furnace. The crucible temperature was maintained considerably lower than the sample temperature to insure no condensation of NaCl on the sample.

Metered oxygen flows were supplied independently to both concentric quartz tubes. Flows were adjusted to gas velocities of 0.7 and 2.5 cm sec^{-1} for the outer and inner quartz tubes respectively. The oxygen supplied to the outer tube could be saturated with water vapor at room temperature by passing the gas through a fritted glass plug in the bottom of a 20 cm high column of water. The mass fraction of NaCl(g) in the apparatus was determined from the weight loss (per unit time) of NaCl(c) in the crucible and the volume flow rate of gas through the apparatus. No attempt was made to apply corrections to the NaCl(g) concentrations for collision and reactions

with the quartz wall of the apparatus. In the target collection experiments a mass fraction of about 50 ppm NaCl(g) was used, and in the mass spectrometric sampling experiments NaCl(g) concentrations of 160 ppm were generally employed. Metal samples were always preoxidized for four hours at high temperature, usually 1000° C in pure oxygen. The experiment was then started by adding contaminant gases, and at least five minutes were allowed to elapse before measurements were begun.

In the target collection experiments, volatile products emanating from the sample were collected on polished platinum targets ($5 \times 5 \times 0.04$ cm) attached to a water cooled copper plate (Fig. 1(a)). The target was positioned about 2 cm above the open end of the quartz tube. A platinum collimator (with a 2 cm diameter opening) was located between the target and quartz tube opening. Deposits collected in measured times were dissolved in water. Resulting solutions were analyzed for metal cations by atomic absorption and/or emission spectroscopy.

Identification of volatile species emanating from samples was accomplished with the high pressure mass spectrometric sampler positioned at the quartz tube opening as shown in Figure 1(b). The high pressure, free-jet expansion, modulated molecular beam, mass spectrometric sampler facilitates direct mass spectrometric analysis of atmospheric pressure sources. This technique preserves the dynamic and chemical integrity of sampled species. The theory and details of the free-jet expansion sampling technique are given in the literature (Refs. 5, 6, 7).

For our sampler the inlet orifice was 0.022 cm in diameter, located at the apex of a 106 degree included angle cone fabricated from 0.025 cm thick Pt 10 % Rh. The cone was welded on the end of a 1.5 cm long by 2.0 cm diameter stainless steel tube. The sampling cone protruded into the quartz tube about 1 cm and was heated to a temperature approaching that of the metal sample. Heating of the orifice was necessary to prevent condensation on and subsequent clogging of the orifice by NaCl and other condensible volatile species.

In the mass spectrometric sampling experiments, the furnace temperature was adjusted to produce a sample temperature of about 1050° C, except in the case of molybdenum. Molybdenum samples were heated to only

675° C because the high rate of vaporization of MoO_3 at higher temperatures resulted in rapid clogging of the sampling orifice. The lower temperature required for molybdenum samples necessitated lower concentrations of NaCl(g) because it was not possible to heat the crucible to higher temperatures without overheating the molybdenum. Generally the NaCl(g) mass fraction was around 4 ppm for molybdenum experiments.

RESULTS AND DISCUSSION

Target collection experiments. - The effects of exposing hot oxidizing metals to partial pressures of NaCl(g), $H_2O(g)$, and NaCl(g) + $H_2O(g)$ was studied for the metal samples Ti, B-1900, Cr, IN-738, VIA, and 731C. For Ti and B-1900 samples no metals (other than Na) were detected in collected deposits. In experiments with the other metal samples, the only metal detected (other than Na) in collected deposits was Cr. The rate of collection of Cr per unit area of sample shall be designated R.

Values of R, obtained with a preoxidized Cr sample exposed to various gas phase compositions, are presented in Table I. These results show that R was increased markedly by additions of $H_2O(g)$ or NaCl(g) to the oxidizing environment. When both of these additions were present simultaneously an additional synergistic effect was obtained. In oxygen alone R = 1 μg cm^{-2} hr^{-1}; the transported Cr was undoubtedly derived from the oxidation of Cr_2O_3 (c) on the surface of the sample to $CrO_3(g)$ (Ref. 8) according to the reaction:

$$Cr_2O_3(c) + \frac{3}{2} O_2(g) = 2CrO_3(g) \tag{1}$$
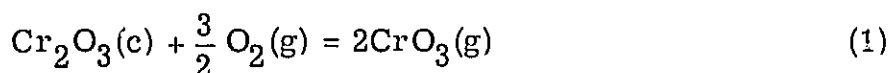
With the addition of $H_2O(g)$ to the oxygen, the value of R was increased by a factor of four. The increase may be attributed to the formation of a volatile hydrated oxide

$$\frac{1}{2} Cr_2O_3(c) + \frac{X+1}{4} O_2(g) + \frac{X}{2} H_2O(g) = CrO_2(OH)_X(g) \tag{2}$$
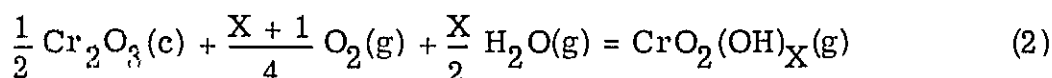
where $X = 1$ or 2. If it is assumed that reactions (1) and (2) occur independently, the value of R due to only reaction (2) was $3 \ \mu g \ cm^{-2} hr^{-1}$.

When only NaCl(g) was added to the oxygen, the value of R increased by a factor of five compared with the case of oxygen alone. This observed increased rate was due to the formation of volatile species containing both Na and Cr (Ref. 3). Again with the assumption of independent reactions, the rate attributable to the Na-Cr-containing species was $4 \ \mu g \ cm^{-2} hr^{-1}$.

Addition of both contaminants, NaCl(g) and H_2O(g), to the oxygen yielded $R = 20 \ \mu g \ cm^{-2} hr^{-1}$. This is twice the sum of the rates of the three individual reactions just discussed. Apparently an additional reaction was occurring; this reaction probably involved NaOH and/or HCl which are expected to be formed by the hydrolysis of NaCl: i.e.,

$$NaCl(g) + H_2O(g) = NaOH(g) + HCl(g) \tag{3}$$
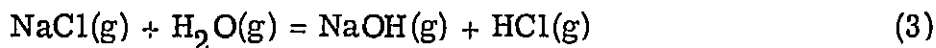
The rate of collection of Cr from preoxidized alloy samples exposed to O_2(g) + H_2O(g) + NaCl(g) was compared with that from oxidized Cr. The results obtained for contaminant additions of 2.5 volume percent H_2O(g) and 50 ppm NaCl(g) are presented in Table II. Except for B-1900, all the alloys tested exhibited volatile Cr-containing species. For IN-738 the value of R was 80 % of that found for pure Cr; for 713C it was 60 %; and for VIA it was 50 %. Measured values of R for 713C and VIA were found to decrease gradaully with each one-half hour collection run. The values reported in Table II are the maximums obtained in the first one-half hour collection run. The observed decreases in R as a function of collection time were probably associated with the rate of diffusion of chromium to the surface and subsequent oxidation to Cr_2O_3. Evidently this process was slower than the reaction to form volatile chromium species at the surface.

Mass spectrometry experiments. - High pressure mass spectrometric sampling techniques were used to identify and measure volatile species emanating from preoxidized samples of Cr and IN-738 at temperatures above 1000° C in oxygen containing H_2O(g) or NaCl(g) or H_2O(g) + NaCl(g). Similar studies were made with Mo samples at 675° C. The main Cr-, Mo-, and Na-containing ions identified under the various experimental conditions are

presented in Tables III, IV, and V together with their measured relative intensities and probably parent molecular species. In all cases, ions were identified by their m/e values, isotopic distribution and behavior when either NaCl(g), H_2O(g) or the sample were removed from the system. The reported relative 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 for each ion, quadrupole mass filter transmission as a function of m/e, and Mach-number focusing factors for each species. At present, most of these quantities are unknown for the complex molecular species presented in the tables. Finally, parent molecular species were assigned on the basis of familiarity with the mass spectrum-molecular composition relationships for other inorganic halide molecule systems. It is well established (Ref. 9) that halogen-containing molecules fragment upon electron impact ionization to yield molecular ions with the loss of a halogen atom: e.g.,
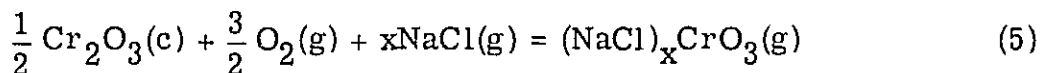
$$Na_2Cl_2(g) + e^- \rightarrow Na_2Cl^+ + Cl + 2e^- \tag{4}$$
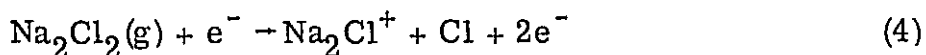
The results presented in Table III are for the Cr_2O_3(c) + O_2(g) + H_2O(g) system; the ion intensities were normalized to a value of unity for the ion O_2^+. The only Cr-containing species identified were $CrO_2(OH)_2^+$ and $CrO_2(OH)^+$. While the ion $CrO_2(OH)_2^+$ could only originate from $CrO_2(OH)_2$ (g), the ion $CrO_2(OH)^+$ could be a fragment of $CrO_2(OH)_2$(g) or it could originate from $CrO_2(OH)$(g). On the basis of these results, it was not possible to determine if $CrO_2(OH)$(g) was actually present. These results are in contrast to the transpiration results reported by Kim and Belton (Ref. 10) for this system. They interpreted their measurements on the basis that $CrO_2(OH)$ was the only volatile oxide in this system.

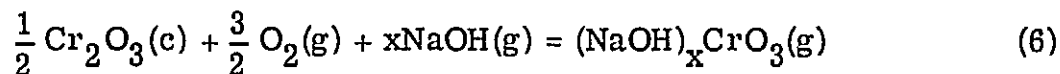In Table IV the results obtained for the Cr_2O_3(c) + O_2(g) + NaCl(g) system, with and without added H_2O(g), are presented. Both sets of ion intensities were normalized to $NaCl^+$ for the system without H_2O(g) added. Such normalization puts the intensities in the proper perspective and shows that addition of H_2O(g) reduces the NaCl(g). The observed Cr-containing species are seen to be mainly complexes of NaCl and CrO_3 with the general formula

$(NaCl)_x CrO_3$ where $x = 1$, 2, and 3. As stated in our previous report (Ref. 3), we believe that these species are the first observed examples of alkali halide-metal oxide complexes. In this regard, one point must be emphasized: the fact that the rate, R, was found to increase in the target experiments when $NaCl(g)$ was added to the $Cr_2O_3(c) + O_2(g)$ system, indicates that R is not limited by the vaporization rate of $CrO_3(g)$ and therefore the Na- and Cr-containing species are not products of gas phase reactions. Furthermore, because species such as $(NaCl)_x CrO_3$ are not the product of gas phase reactions they likewise cannot be the product of sampling artifacts such as clustering (Ref. 11).

Returning to Table IV, one se s that the main effects of adding $H_2O(g)$ to the $Cr_2O_3(g) + O_2(g) + NaCl(g)$ system were: (1) to reduce the $NaCl^+$ intensity, and (2) to increase the prominence of $NaOH-CrO_3$ complexes. Both effects could result from the formation of NaOH in the hydrolysis of NaCl, either by reaction (3) or on the surface. The point emphasized above applies equally to the observed complex $(NaOH)_x CrO_3$ where $x = 1$ and 2. The fact that NaOH-containing species were observed even when $H_2O(g)$ was not added to the system indicates that the system was not completely free of water vapor. No special precautions were taken to dry the oxygen or sodium chloride used in these experiments. Parent ions corresponding to the species $NaOH(g)$ and $HCl(g)$ could not be measured because large in-phase background peaks were present at their respective m/e. These background peaks were due to the approximately 2300 ppm of argon impurity in the "missile" grade oxygen used.

An exhaustive search was made for the frequently proposed (Refs. 2, 4, 12-17) vapor molecules CrO_2Cl_2, $CrCl_2$, $CrCl_3$ and Na_2CrO_4. This effort was unrewarding and only the species $Na_2Cr_2O_7(g)$ was detected in addition to the complexes. Therefore, we conclude that the main reactions responsible for the vapor transport of Cr are:

$$\frac{1}{2} Cr_2O_3(c) + \frac{3}{2} O_2(g) + xNaCl(g) = (NaCl)_x CrO_3(g) \tag{5}$$

$$\frac{1}{2} Cr_2O_3(c) + \frac{3}{2} O_2(g) + xNaOH(g) = (NaOH)_xCrO_3(g) \tag{6}$$

where $x = 1, 2$, and 3 for reaction (5), and $x = 1$ and 2 for reaction (6).

Experiments were performed with samples of IN-738 at about 1050° C in $O_2(g)$ + NaCl(g). Mass spectral scans were made over the range from $m/e = 23$ to $m/e = 250$. All of the ions in this range listed in Table IV for the $Cr_2O_3(c)$ + $O_2(g)$ + NaCl(g) system were detected with IN-738. Additional, as yet unidentified peaks of lesser intensity were recorded at m/e values of 65, 66, 88, 89, 105, 107, 146, and 147. That the main species observed with IN-738 correspond to those noted with Cr is not surprising because it is well established (Ref. 18) that the main surface oxide constituent present on oxidized IN-738 is $Cr_2O_3(c)$.

Because Mo is a member of the same family as Cr, and because Mo has been identified near the surface in certain oxidized alloys (Ref. 18), we investigated the Mo system to ascertain if the same type of complex molecules were formed as observed with the Cr system. Results obtained for the $MoO_3(c)$ + $O_2(g)$ system, with and without additions of NaCl(g) and $H_2O(g)$, are presented in Table V. Without any contaminants added to the oxygen, the primary vaporizing species was $(MoO_3)_3$ as one would expect (Ref. 19). The other ion intensities were normalized to a value of unity for the $(MoO_3)_3^+$ ion. The tetramer $(MoO_3)_4$ was also observed but at about $1/3$ the intensity relative to the trimer. With NaCl(g) added to the oxygen, mixed alkali halide-metal oxide complexes became prominent. These complexes are similar to those found for chromium and they can be represented by the general formula $(NaCl)_x(MoO_3)_3$ where $x = 1$ and 2. These complexes differed from the chromium ones in that the metal oxide was polymerized in keeping with the characteristic difference between Cr- and Mo-oxide systems at high temperatures (Refs. 8 and 19). Additions of $H_2O(g)$ alone to the oxygen resulted in the formation of the hydrated oxide molecule $MoO_2(OH)_2(g)$, postulated by Belton and Jordan (Ref. 20). This species was quite abundant judging from the fact that the ion intensity was five times greater than the trimer ion. The ion $MoO_2(OH)^+$ was also observed but as with the chromium case it was not possible to decide whether this ion arose from ionization of $MoO_2(OH)(g)$ or from fragmentation of $MoO_2(OH)_2(g)$.

When both NaCl(g) and H_2O(g) were added to the oxygen with Mo samples, the molecule $NaOH(MoO_3)_3$ was observed in addition to those noted for O_2 alone, NaCl(g) alone and H_2O(g) alone. In this case it was not possible to discern if the species $Na_2OH(MoO_3)_3^+$ was present because of interference from the species $NaCl(MoO_3)_3^+$.

CONCLUDING REMARKS

The mass spectrometric identification of the vapor species emanating from the metal samples studied under various conditions allows a better interpretation of the rates obtained for chromium vaporization (Table I) in the target collection experiments. For oxygen without any contaminant additions, the volatile chromium species was undoubtedly CrO_3(g) formed by reaction (1). This species was not identified in our mass spectrometric sampling because its concentration (at the highest temperatures we could achieve with our furnace) was just below the detection sensitivity of our sampling system. The concentration, as calculated from measured R values and gas flows, was about 0.03 ppm, and the detection limit at this mass was around 0.05 ppm.

With H_2O(g) added, the rate increased because of the formation of $CrO_2(OH)_2$(g), in addition to the CrO_3(g), according to reaction (2) with x = 2. Additions of NaCl(g) yielded increased rates by the formation of $(NaCl)_xCrO_3$(g) with x = 1, 2, and 3 according to reaction (5). With the additions of H_2O(g) + NaCl(g), the rate R was observed to increase more than expected from the sum of reactions (1), (2), and (5). The difference must arise from the formation of $(NaOH)_xCrO_3$(g) (with x = 1 and 2) by reaction (6). Thus we can conclude that NaOH molecules are more reactive than NaCl molecules because the rate of Cr transport was higher when some of the NaCl was converted to NaOH.

With regard to the chromium system (and certain alloy systems also) it is important to reiterate that the observed enhanced vaporization of chromium precludes a gas phase reaction explanation of the formation of

the complex molecular species reported here. A gas phase mechanism would be limited by the rate of formation of $CrO_3(g)$.

In the experiments involving molybdenum the observed vaporizing species were seen to be analogous to those found for the chromium system except that the Mo-containing species displayed the stronger tendency of molybdenum to form oxide polymers. The molybdenum results stimulate one to speculate about tungsten because it is in the same chemical family as Cr and Mo. One would expect that tungsten would form complex molecules identical to those formed by Mo in our experiments but probably at higher temperatures. Unfortunately, such W-containing molecules were beyond the mass range of our mass spectrometer.

A more quantitative correlation of these results is not possible at this time because we have not derived actual partial pressures for the various species from the measured ion intensities. Nevertheless, the qualitative description provided by our results provide valuable insights into the hot corrosion process.

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TABLE I. – RATE OF COLLECTION OF CHROMIUM
VOLATILIZING FROM CHROMIUM SPECIMEN EX-
POSED TO ONE ATMOSPHERE OF SLOWLY FLOW-
ING OXYGEN CONTAINING DIFFERENT VAPORS

Chromium temperature, T_{cr}, in ^{o}C	Mass fraction $H_2O(g)$,[a] %	Mass fraction $NaCl(g)$,[b] ppm	Rate collection,[c] $\mu g\ cm^{-2}\ hr^{-1}$
1000	0	0	1
1000	1.4	0	4
1000	0	50	5
1000	1.4	50	20

[a]Oxygen was saturated with $H_2O(g)$ at 21° C by bubbling through fritted glass into a 20 cm column of water.

[b]The mass fraction of $NaCl(g)$ was determined from weight loss of the platinum crucible and from the gas flow through the apparatus. No corrections were made for collision and reaction with the quartz walls.

[c]Measured collection rates were reproducible to ±20 %.

TABLE II. – RATE OF COLLECTION OF CHROMIUM
VOLATILIZING FROM CHROMIUM AND CHROMIUM-
CONTAINING ALLOYS EXPOSED TO ONE ATMOS-
PHERE OF SLOWLY FLOWING OXYGEN CON-
TAINING 2.5 vol. % $H_2O(g)$ AND 50 ppm NaCl(g)

Material	Temperature, ^{o}C	Rate of collection, $\mu g \ cm^{-2} hr^{-1}$
Chromium	1000	15
IN-738	1015	12
713C	1015	10[a]
B-1900	1015	0
NASA-TRW VIA	1015	7.5[a]

[a]Rates were falling slowly in time. Value given
   is maximum rate determined in first one-half
   hour run. It was not possible to assess the
   reproducibility of the rate.

TABLE III. - MASS SPECTRUM OF VAPORS OVER THE

$Cr_2O_3(c) - O_2(g) - H_2O(g)$ SYSTEM

Ion	Relative intensity	Probable parent molecule
O_2^+	1.00	O_2
$CrO_2(OH)^+$	2×10^{-8}	$CrO_2(OH)$ and/or $CrO_2(OH)_2$
$CrO_2(OH)_2^+$	3×10^{-8}	$CrO_2(OH)_2$

[a]$Cr_2O_3(c)$ sample temperature = 1100° C; O_2 flow = 380 ml/min; H_2O saturated O_2 at 21° C.