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D. Caplan and M. Cohen

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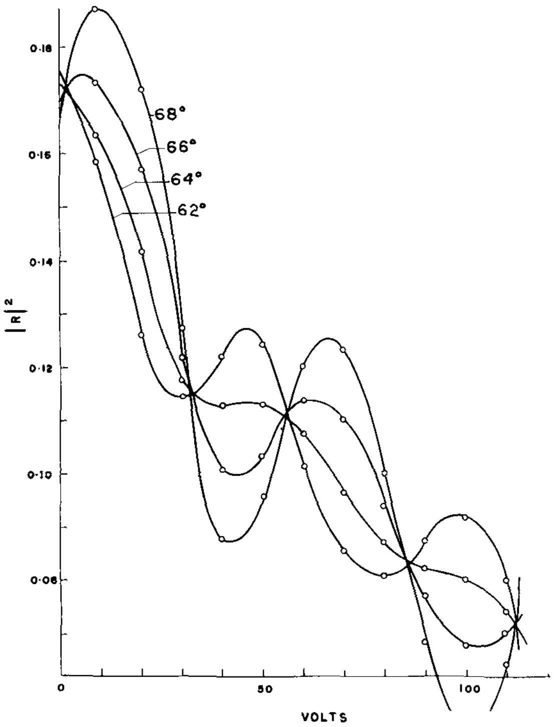

Fig. 20. Reflectivity vs. voltage of formation at 10 ma cm^{-2} and 25°C for zirconium.

Discussion

The direction of the dependence of the refractive index on the conditions of formation is somewhat surprising, since, according to present theories, it means that the index is higher the lower the concentration of mobile ions, *i.e.*, of Frenkel defects.

The explanation of the thin outer layer of absorbing oxide is at present uncertain. It certainly seems to be significant that the thin absorbing layer present in films formed in dilute solution becomes a thick layer in films formed in concentrated solution. It is tempting to assume that this layer represents a transitional layer in which the adjustment is made between the kinetics of the oxide/solution interface and those of the electrically neutral oxide in the interior of the film. However, the effect could be due to some more trivial cause, such as the adsorption of SO_4^{-2} by the outer layers of oxide. It is worth noting that to account for accurate reflectivity measurements it has usually been required to introduce the idea of transitional layers in which, for example, the refractive index varies through the outer few angstroms of the reflecting material.

Acknowledgments

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The Volatilization of Chromium Oxide

D. Caplan and M. Cohen

Division of Applied Chemistry, National Research Council, Ottawa, Canada

ABSTRACT

The phenomenon of evaporation of chromium oxide from chromium alloys oxidized at high temperatures was investigated by observing the loss in weight when Cr_2O_3 pellets were heated at 1000°-1200°C in various atmospheres. Appreciable volatilization occurred in oxygen, more in wet oxygen, but none in argon or wet argon. Fe_2O_3 specimens showed volatilization in none of these atmospheres. The results indicate that evaporation occurs by oxidation of Cr_2O_3 to gaseous CrO_3 which dissociates to Cr_2O_3 on redeposition. The mechanism by which moisture promotes volatilization was not established.

When Cr alloys are oxidized at high temperatures, it has sometimes been observed that Cr_2O_3 crystals deposit at cooler parts of the apparatus (1-4), indicating that Cr or its oxide somehow evolves from the specimen and is transported through the gas phase. This is surprising in that the barrier film of refractory oxide covering the specimen would be expected to prevent such an effect. Interpretation of the kinetics of oxide film thickening from weight gain/time measurements is thus complicated since a weight loss is superimposed on the weight gain of oxygen which supposedly is being measured. In addition, it is likely that the characteristics of the film as a diffusion barrier are affected.

Neither the vapor pressure of Cr_2O_3 nor its dissociation pressure is high enough to account for the quantities of deposit observed. Because of the known high vapor pressure of Cr it was at first considered that the metal itself escaped in some manner. The authors proposed (1) that Cr_2O_3 was reduced to Cr at the outer surface by the carbon of the alloy. When volatilization was observed with essentially carbon-free alloys it seemed necessary to invoke a mechanism whereby Cr evaporation takes place because the oxide film fails to act as a proper barrier layer, perhaps by rapid diffusion of Cr along oxide grain boundaries or escape at real discontinuities in the film (5). But when it was learned that Cr_2O_3, in the absence of metal, lost weight when heated in oxygen (6) it became evident that a volatile oxide was being formed.

To investigate the effect, Cr_2O_3 was heated in flowing oxygen and argon and the weight loss measured. Parallel experiments were performed with Fe_2O_3. The loss in weight was determined also in moist oxygen and argon since moisture had previously been shown to affect the oxidation rate of Cr alloys (1, 7). In addition, Cr_2O_3 was formed from metal in the same atmospheres and examined by x-ray diffraction and infrared absorption spectroscopy to see if moisture modified the oxide structure.

Experimental

Pellets 1.2 cm in diameter and 1.2 cm high were pressed from reagent grade Cr_2O_3 and Fe_2O_3 and sintered at 1400° in air or oxygen to about 98% of theoretical density. Chromium metal was U.S. Bureau of Mines 0.015-in. sheet.

The specimens were suspended in a vertical tube furnace, 2.9 cm ID, up through which purified oxygen or argon at 1 atm flowed at rates regulated between 10 and 200 ml/min. The gases were used dry or saturated with water at 25° at which temperature the vapor pressure of water is 24 mm. Runs were at 1100° and 1200° except for one at 1000° in still air. Table I summarizes most of the runs carried out. The oxide pellets were held in a high-purity alumina crucible cut in an openwork pattern to expose them to the flowing gas. Runs were started by lowering the specimen into the hot zone slowly to avoid loss of weight by spalling. Although weight loss *vs.* time curves were obtained with a recording automatic balance only the final, total weight changes are reported since up to 40% of the evolved product condensed back on to the suspension system.

The Cr sheet samples were oxidized in similar fashion for such times, 5-100 hr, as to give oxide films 1-10μ thick. (The weight gain/time curves recorded by the automatic balance will be reported subsequently in connection with the scaling of Cr alloys.) In this range of thickness the Cr_2O_3 absorbed infrared radiation in the proper amount to yield an absorption spectrum when a method of reflection at 90° incidence was used. Spectra were also obtained by transmission through mull samples prepared from finely ground separated oxide.

In an additional experiment[1] an oxy-gas torch was directed at the surface of sintered Cr_2O_3 and the small amount of smoke evolved caught on a cold support. The surface temperature of the Cr_2O_3 was approximately 2000°C. The product was examined by reflection electron diffraction.

Results

Figure 1 shows the effect of atmosphere on the volatilization of Cr_2O_3 at 1100° and 1200° and a gas flow rate of 200 ml/min. At this flow rate moisture

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[1] Suggested by discussion with R. M. Fowler of Union Carbide Metals Corp. when this work was presented at the ECS Houston meeting, October 1960.

Table I. Weight loss on heating Cr_2O_3 and Fe_2O_3 in various atmospheres

Run	Specimen	Temp, °C	Gas	Time, hr	Gas flow ml/min	l	Weight loss mg	mdd	μg/l
1	Cr_2O_3	1000	still air	72	—	—	0.3	1.5	—
2	Cr_2O_3	1100	oxygen, dry	65	10	39	0.9	5	23
3	Cr_2O_3	1100	oxygen, dry	19	200	230	0.8	15*	3.5
4	Cr_2O_3	1100	oxygen, dry	20	200	240	0.6	11	2.7
5	Cr_2O_3	1100	oxygen, wet	20	200	240	2.1	38*	8.9
6	Cr_2O_3	1200	argon, dry	66	200	792	0	0	0
7	Cr_2O_3	1200	argon, dry	115	192	1300	0	0	0
8	Cr_2O_3	1200	argon, wet	20	192	230	0	0	0
9	Cr_2O_3	1200	oxygen, dry	20	10	12	2.1	37	173
10	Cr_2O_3	1200	oxygen, dry	20	10	12	1.3	24	111
11	Cr_2O_3	1200	oxygen, dry	20	20	24	1.8	33	77
12	Cr_2O_3	1200	oxygen, dry	20	200	240	2.3	41	10
13	Cr_2O_3	1200	oxygen, dry	20	200	240	2.6	45	11
14	Cr_2O_3	1200	oxygen, dry	42	200	504	8.0	68*	16
15	Cr_2O_3	1200	oxygen, wet	20	10.2	12.2	1.9	33	152
16	Cr_2O_3	1200	oxygen, wet	20	63	76	3.3	58	43
17	Cr_2O_3	1200	oxygen, wet	20	200	240	5.6	99	23
18	Cr_2O_3	1200	oxygen, wet	20	200	240	6.0	106*	25
19	Fe_2O_3	1200	oxygen, dry	20	200	240	0	0	0
20	Fe_2O_3	1200	oxygen, wet	20	200	240	0	0	0
21	Fe_2O_3	1200	oxygen, wet	65	200	240	0	0	0

* Plotted in Fig. 1.

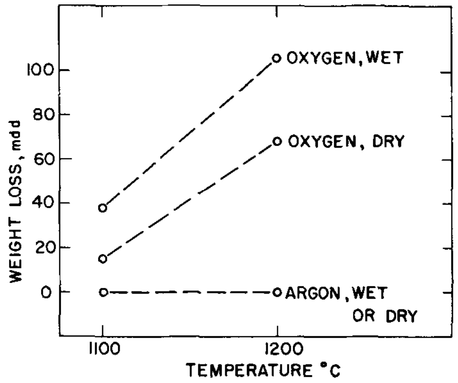

Fig. 1. Weight loss of Cr_2O_3 in wet and dry oxygen and argon at 1100° and 1200°C; Flow rate 200 ml/min.

approximately doubles the rate of weight loss in oxygen. No loss occurs in argon, either wet or dry. With Fe_2O_3 (Table I) no loss occurs in wet or dry oxygen.

The variation in evaporation rate with oxygen flow rate is shown by the results in Table I, which includes the data of Fig. 1. Expressing the weight loss in micrograms per liter of gas flowed (last column), it is seen that as the flow rate is decreased the numbers increase as they should (*e.g.*, runs 9-14, 15-18, or 2-4) but that a constant value is not obtained, as should be the case if the saturation pressure of the volatile species were to be determined (8, 9). Furthermore, nonsystematic variations appear *e.g.*, the loss in run 9 is greater than in run 10. This occurred because run 9 immediately followed four 1200° runs with Fe_2O_3 in oxygen during which the Cr_2O_3 which had been condensed in the apparatus from previous runs was evaporated away. In run 9, therefore, only the specimen itself was contributing the volatile material to the flowing gas and a higher (and more nearly correct) weight change was observed. This applies also to runs 14, 15, and 18. Otherwise some evaporation occurs from Cr_2O_3 deposits as well as from the pellet, but is not recorded as part of the weight loss. It follows that the experimental design is not satisfactory for the accurate determination of vapor pressure or that the transportation method is not applicable to the Cr_2O_3-O_2-H_2O system.

Infrared absorption spectra of adequate quality were obtained from the thin oxide films on Cr sheet by the normal incidence, single reflection method, as well as with the more conventional mull samples. Absorption maxima were observed at 680, 850, 930, 980, 1100, and 1160 cm^{-1}. No differences in the spectra could be detected between Cr_2O_3 formed in dry oxygen, wet oxygen, or argon containing 20 ppm oxygen.

X-ray diffraction of these same three Cr_2O_3 samples and also of Cr_2O_3 condensed on the suspension system from Cr_2O_3 heated at 1200° in wet oxygen (run 17) disclosed no significant difference in the interplanar spacings; the variation was no more than 1 part in 10,000.

Electron diffraction of the smoke developed by directing an oxy-gas torch onto Cr_2O_3 showed this condensate to be CrO_3. Sufficient material could not be produced to confirm this by x-ray diffraction.

Discussion

The observation that no loss of Cr_2O_3 occurs in argon confirms the fact that volatilization is not by dissociation of the oxide nor as Cr_2O_3 vapor. Since weight loss does occur in oxygen, the volatile species must be a higher oxide of chromium. Fe_2O_3 shows no volatilization, presumably because no oxide of appreciable vapor pressure forms, and none is known. CrO_3 is a known volatile oxide of Cr, but it exists normally only at lower temperatures so that, at the temperatures and oxygen pressures of the present work, oxidation of Cr_2O_3 to CrO_3 is thermodynamically unfavorable. However, the reaction to form gaseous CrO_3

$$Cr_2O_{3(s)} + 3/2\ O_{2(g)} = 2CrO_{3(g)} \qquad [1]$$

would have in its favor the increase in entropy associated with the extra half mole of gaseous product, and therefore a less unfavorable free energy change. Furthermore, in a dynamic system with a considerable flow of gas, appreciable material transport can occur even from a rather small equilibrium partial pressure.

Taking the largest experimental value of weight loss per liter of gas flowed, which is to say the most nearly correct value, run 9, a Cr_2O_3 loss of 173 $\mu g/l$ corresponds to a CrO_3 partial pressure of 5.1×10^{-5} atm. If this represented saturation, the equilibrium constant

$$K_p = \frac{(P_{CrO_3})^2}{(P_{O_2})^{3/2}} \qquad [2]$$

becomes 2.6×10^{-9}, equivalent to $\Delta F°_{1473} = +29$ kcal. In fact, saturation has not been demonstrated so that K_p is too small and $\Delta F°$ too large by an unknown amount, although the error may not be very large. But the main point of the foregoing is that CrO_3 may be reasonably considered as the volatile species despite its instability. This observation of hexavalent Cr oxide is consistent with an explanation offered in a previous publication (10) to account for an anomalous sharp minimum in the cathodic reduction curves of oxide films on Cr alloys. The proposal was made that Cr_2O_3 films formed under strongly oxidizing conditions were defect oxides containing appreciable Cr^{6+} ion and would be properly described as $Cr_{2-2x}^{3+}\ Cr_x^{6+}\ \Box_x\ O_3$ where $\Box_x$ represents the concentration of cation vacancies. The latter would be larger the higher the oxygen pressure and the lower the temperature.

The Cr smoke experiment lends strong support to the CrO_3 hypothesis. That CrO_3 actually was condensed must be ascribed to the gas quenching that the volatilized Cr oxide receives as it is swept out of the oxy-gas flame. In all other cases the CrO_3 vapor decomposes to Cr_2O_3 and oxygen by the reverse of equation [1]. Hence, in the flow experiments only Cr_2O_3 is detected by x-ray diffraction in the sublimate on the furnace tube and suspension system. [In some work which had not appeared in print at the time that this paper received its final revision, CrO_3 had been detected mass spectrometrically as a gaseous species when Cr_2O_3 was heated under oxidizing conditions (26).]

The accelerating effect of moisture cannot be elucidated from these experiments. The attempts by x-ray diffraction and infrared spectroscopy to demonstrate the presence of hydrogen in Cr_2O_3 heated or formed in moist gas were not successful; one can say that large quantities do not incorporate themselves in the solid oxide lattice. The vaporization of some nonvolatile oxides in the presence of moisture has been shown to be due to the formation of gaseous hydrates. This is so with Li_2O (11, 12), B_2O_3 (13), BeO (14-17), and perhaps Al_2O_3 (17), WO_2, W_4O_{11}, WO_3, MoO_3 (18) and some others (19). But the Cr_2O_3 case is different in that the wet argon experiment in which no volatilization occurred showed that a hydrate of Cr_2O_3 does not form. It may be that volatilization is enhanced by formation of a gaseous CrO_3 hydrate, but there is as yet no evidence in support of this. Where a volatile hydrate forms and no volatile oxide exists the situation appears quite straightforward. But where volatile oxides are present, U, Mo, Cr, Si, Pt, the function of water has not been demonstrated unequivocally.

Alternatively, moisture may increase volatility by stabilizing gaseous polymers. Mass spectrometric observations have shown rather surprisingly that the high-temperature volatile species over such oxides as WO_3, MoO_3, BeO, and GeO are polymers as high as pentamers (20, 21).

Third, moisture may, by changing the activation energy, act as a promoter for the surface oxidation reaction, perhaps facilitating removal of the oxidized product from the surface. The results at the slowest flow rate suggest such a catalytic effect: the weight loss in wet oxygen was not greater than in dry oxygen (run 15 *vs.* run 9). If the gaseous hydrate or polymer idea were valid, the weight loss should be greater with moisture at the slow flow rate also. But because of the aforementioned inadequacies of the transportation method for the Cr_2O_3-O_2-H_2O system, the data at low flow rates are variable and a definite conclusion cannot be drawn.

Having established the conditions under which Cr_2O_3 evaporates one can recognize instances where the effect of such evaporation should be considered. The spurious kinetic results that can arise in studies of oxide film growth on Cr alloys at high temperatures were mentioned at the beginning. A corollary is that moisture might appear to inhibit or promote high-temperature oxidation depending on whether the measurements were of gain in weight of oxygen or loss in weight after removal of oxide. For example, the weight gain/time curves of the Cr panels used to form Cr_2O_3 films show smaller parabolic rate constants in moist oxygen than in dry oxygen, in an amount that could be accounted for by the more rapid volatilization in wet oxygen rather than by a change in film growth kinetics. In alloys, where oxides of more than one metal occur, the composition of the outermost layer especially would be depleted in Cr oxide by the evaporation.

Spurious results can occur also in chemical analysis where materials containing Cr are ignited in air. In the chemical analysis of passive films separated from stainless steel, moisture contents up to 30% were deduced (22) on the basis of the decrease in weight that occurred when 100 μg or smaller samples were ignited at 1000°. A possible alternative explanation is that Cr_2O_3, not H_2O, was driven off in the ignition. If so, the suggestion that passive films have gel-like characteristics loses support. Attempts in this laboratory to confirm the presence of water in passive films prepared similarly have not succeeded. The reported permeability of Cr_2O_3 films for Cr (5) might also be explained as oxide volatilization.

In the mixed oxides that form protectively on heat resistant alloys containing Cr, the volatility of Cr oxide may be less than from Cr_2O_3, either because of a crystallographic difference (spinel instead of rhombohedral), dilution, or the valence compensation effect (23) by which, for example, the evaporation of uranium oxide is depressed by inhibiting the oxidation of UO_2 to UO_3. If this is so, a mixed oxide in some atmospheres and temperatures could be preferable to pure Cr_2O_3 in spite of a less ideal defect structure which may permit more rapid diffusion. There is some literature evidence in this direction (24), but the situation is not yet clear.

To summarize, Cr_2O_3 is shown to volatilize but only in an oxidizing atmosphere. Moisture increases the rate of evaporation in some way not yet understood. Fe_2O_3 does not volatilize. CrO_3 is thermodynamically reasonable as the gaseous species, can be gas-quenched out of hot Cr oxide smoke, and is believed to account satisfactorily for the evaporation of Cr oxide. Normally it dissociates to Cr_2O_3 on redeposition. Identification of CrO_3 in the vapor phase and an explanation of the moisture effect requires additional information: application of the Knudsen effusion method in which the high-temperature gaseous product is viewed with a mass spectrometer (13, 23) seems ideally suited to this purpose. Incorrect interpretation may be attached to high-temperature processes involving Cr oxide if its volatility is not recognized.

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Electrolytic Etching of Dense Tantalum

A. L. Jenny and R. A. Ruscetta

Capacitor Department, General Electric Company, Irmo, South Carolina

ABSTRACT

A practical method of etching dense tantalum for the purpose of magnifying its effective surface area is described. The degree of surface area magnification is related to such parameters as electrolyte composition, anodic current density, temperature, and characteristics of metal specimens to be treated. The decrease in surface area magnification as a function of postetch anodizing voltage apparently signifies the filling in of certain etch pits with tantalum oxide and gives a clue to the size of these pits.

Tantalum metal of capacitor quality is a powder metallurgy product of relatively high purity. The metal in a variety of forms such as porous sintered compacts, wire, sheet, and foil is being used in substantial quantities in the manufacture of high-quality tantalum electrolytic capacitors.

The present investigation is concerned with the magnification of the capacitance value of plain tantalum foil to the greatest extent possible by a practical and economical etching treatment.

Magnification of capacitance.—The equation which characterizes the electrical capacitance of a parallel plate capacitor is equally valid for an electrolytic capacitor.

$$C = (K A)/T \qquad [1]$$

wherein C is capacity; K a dimensional constant which includes ϵ, the specific inductive capacitance; A area of electrodes; T distance between plates.

In an electrolytic capacitor, T is the thickness of the anodic oxide film which is directly proportional to the formation voltage and to the absolute temperature. Hence, we may now write

$$C = (K' A)/E \qquad [2]$$

In Eq. [2] K' is a temperature-dependent function having the units of volt microfarads per cubic centimeter when C is expressed in microfarads and the cgs system is used dimensionally. The experimental values of K' for unetched tantalum foil are approximately 25 and 21, respectively, for formation temperatures of 25° and 95°C.

As predicted by Eq. [2] when plain and etched specimens of foil are anodized (formed) to the same voltage and at the same temperature, the increase in surface area achieved by etching will be manifested by a proportional increase in the measured capacitance.

The ratio of the capacitance per unit of projected area of an etched specimen to that of a plain specimen is termed the capacitance ratio or etch ratio. To define the etch ratio completely, both the anodizing voltage and temperature must be specified. In this paper the voltage is 75 ± 1 v d.c. and the temperature is 25° ± 2°C unless otherwise specified.

Etching process-general.—Several U. S. patents have been issued relating to etching processes to increase the effective area (and therefore the capacitance) of tantalum specifically for electrolytic capacitor purposes. Kahan (1) uses aqueous solutions of concentrated HF and HCl in an electrolytic system, Houtz (2) reacts tantalum with chlorine at 350°-400°C, Jenny (3) etches electrolytically in a substantially nonaqueous system containing fluoride salts, and Ruscetta and Jenny (4) use an essentially nonaqueous electrolyte containing a variety of salts.

The inherent properties of tantalum render it generally unresponsive to the usual chemical and electrochemical etching techniques. For example, the rapid embrittlement of tantalum by hydrogen even at room temperature precludes the use of chemical etchants which liberate hydrogen such as hydrofluoric acid alone or mixed with other acids or solutions of ammonium bifluoride. This is particularly true when treating thin gauge foils which must be wound subsequently on small diameter arbors, the so-called winding process in the manufacture of electrolytic capacitors. Furthermore, the ease with which tantalum acquires an insulating film when polarized anodically in most aqueous solutions represents a distinct departure from normal electrolytic etching procedures.