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The Morphology of Oxide Reduction: Chromic Oxide

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The mechanism of the high shrinkage that occurs in chromic oxide in reducing conditions has been investigated by micrographic, analytical, electrical resistance, and other means. The effect of the reducing conditions is to modify the surface of the oxide particles, the core remaining normal oxide (i.e. oxygen excess). The modification is predominantly a change to a lower oxide or oxides and/or metal, although transitional formation of oxygen-deficient oxide is implied. In oxidising conditions (which cause fritting, but not shrinkage), modification to the extent that surfaces become of approximately stoichiometric proportions also occurs, but this change is apparently caused by loss of trioxide and results in unreactive oxide.

Types of electrical resistance test employed include (i) constant low-temperature, variable-oxygen, p/n tests on compacts and powders, and (ii) variable-temperature tests across a compact surface, across a fracture, and across chromium trioxide undergoing decomposition.

Additionally, chromium trioxide has been decomposed to chromic oxide over the range 400 to 1400° C, in argon and in oxygen. The apparent O/Cr ratio decreases on decomposition at 1400° C, particularly markedly in an oxygen atmosphere, and is accompanied by a drastic reduction in reactivity.

1. Introduction

The work to be described had its origin in an investigation into a new method of making cermets, which consisted in heating compacted mixtures of finely divided oxide and carbon (sufficient for partial reduction) at elevated temperatures and reduced pressures. Particularly high shrinkage was found in oxide-rich chromic oxide compositions. The experimental conditions necessary to produce maximum shrinkage were established [1], and further investigations [2, 3] showed that the shrinkage could also be induced by additions of either chromium metal, silicon, or hydrogen, in place of carbon, i.e. by reducing agents generally.

Two processes probably contribute towards the shrinkage. The presence of broad reaction haloes in diffusion-couple experiments [3], in conjunction with evidence of high vapour pressure of chromium during sintering, suggests that rapid permeation and coating of the oxide particles occurs at an early stage [4], but this process alone would not explain the shrinkage. Kramers and Smith [5] considered that increased diffusion resulted from a reduction of the O/Cr ratio below the stoichiometric value. However, the present investigation showed that, whereas the particle surfaces are modified, the bulk oxide remains normal (p-type). This emphasises the desirability of studies of specimen morphology in addition to overall kinetic measurements [6-8].

As in previous work [1, 2], cold compaction and sintering at 1430° C was standard procedure. The base was chromic oxide of laboratory-reagent grade, unless otherwise stated; other reagents were generally of comparable purity.

2. Experimental Method

The word cermet will be used as a convenient abbreviation for oxide which has undergone high shrinkage as a result of the processes already indicated; oxide with no addition will be referred to as plain oxide. Powder mesh gradings refer throughout to British Standard specifications.

Free chromium was shown up on polished sections under ordinary light. Examination by reflection under crossed nicols differentiated between what will be termed "un-altered" and "altered" oxide.

The free chromium content of sintered chromic oxide and of two cermets was determined by a method depending on the insolubility of fired oxide in hot dilute HCl [9, 10]. 1 g powder was boiled gently with 100 ml 10% HCl for 30 min, cooled, filtered through a pulp pad, and washed with 4% HCl. 8 ml concentrated H_2SO_4 was added to the filtrate which was then evaporated to fumes, diluted to 100 ml, and the Cr content determined by the standard persulphate-ferrous ammonium sulphate method.

A plain oxide and low-carbon cermet powder were examined by X-ray diffraction (Cu-Kα lines, 9 cm Unicam camera).

Indirect information on changes in O/Cr ratio with calcination temperature was obtained by reacting oxide (previously prepared by the heating of chromium trioxide in either oxygen or argon) with a known amount of carbon ($\frac{1}{4}$%) and estimating by metallographic examination the free chromium produced. The assessment was by count of chromium particles on a standard-size polished area.

Increase in the oxygen pressure results in an increased conductivity with a p-type semiconducting oxide, and a decreased conductivity with an n-type. Numerous investigations [11-18] have thus shown that chromic oxide is p-type, although it is suggested [13, 14] that it becomes amphoteric above 1250° C. The present interest is in investigating the morphology of sintered compacts by conductivity measurements, and the direct current method was used which tends to emphasise particle surface effects [19].

Two platinum wires $\frac{1}{8}$ in. (3 mm) apart were laid parallel along the bottom of an alumina boat and were connected directly to a dc resistance meter ("Avometer"). The instrument was in circuit only when readings were taken; reversal of polarity made no difference to the reading. The sample (powder or unbroken compact) was placed over the wires, the assembly was transferred to a tube furnace and the resistance of the sample measured with argon and oxygen flowing alternately. The gases were dried with silica gel and the flow was slow and constant. The temperature of test (not to be confused with the sintering temperature and the calcination temperature) was standardised at 500° C; this was the lowest that could be employed, compatible with adequate sensitivity. The technique just described was used for the main electrical tests; in additional tests, variations (e.g. in temperature) were made as will be indicated.

3. Results

3.1. Microscopy and Analysis

Plain oxide appeared green (i.e. unaltered in the terminology defined in section 1) to the eye and under crossed nicols; viewed similarly, the cermet matrix was largely black (altered). Ordinary microscopic illumination showed up both constituents as a dull white. Fig. 1 illustrates the terminology used: two chromium particles, A (rendered visible by a superimposed second exposure without nicols), are surrounded by reaction haloes of altered oxide, B. C is a band of unaltered oxide. The typical appearance of cermet fractures under crossed nicols was a conglomerate of unaltered and altered oxide. This is illustrated by fig. 2 showing the appearance of a hardness impression, D, on a cermet. The bright fracture area, E, around

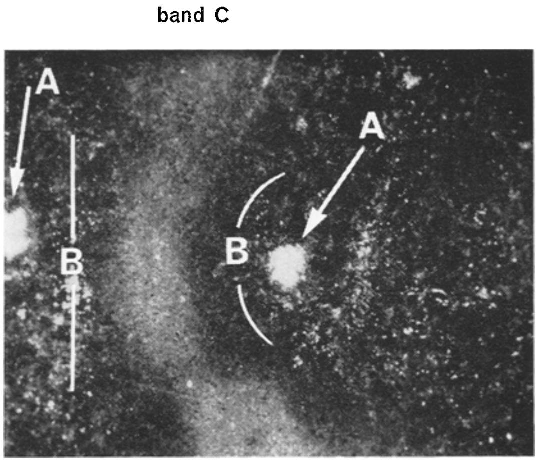

Figure 1 Photographed under crossed nicols. A: chromium particles; B: haloes of altered oxide; C: band of unaltered oxide. (×35)

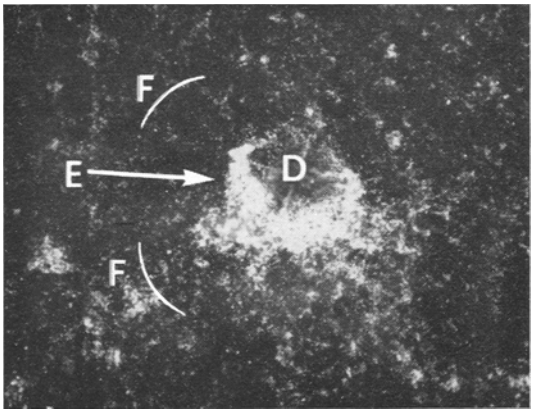

Figure 2 Photographed under crossed nicols. D: centre of impression; E: bright fracture face of unaltered oxide; F: matrix. (×70)

the impression shows unaltered oxide, whereas the directly impacted area remains dark like the matrix. When cermets are ground in a mortar, the first crushings are green, but with further grinding the mass becomes first darker and finally a lighter colour again; −350-mesh powder appears green under crossed nicols.

The compositions and the chemical analyses are recorded in table I. The chromium equivalent was calculated on the assumption that the equation $Cr_2O_3 + 3C = 2Cr + 3CO$ applied. There is fair agreement between calculated and actual for the high chromium sample. With the nominal $\frac{1}{4}$% there is no agreement; clearly most of the addition is ineffective in producing metallic chromium.

TABLE I Analysis for free chromium.

Graphite added (%)	Chromium equivalent of graphite (%)	Chromium actually found (%)
nil	nil	0.028
0.253	0.733	0.138
2.60	7.52	7.07

In the X-ray analysis, the plain oxide and the cermet gave only a chromic oxide pattern.

Table II shows the chromium content estimated metallographically (section 2), and various other properties of the sintered compacts, as a function of calcination temperature.

3.2. Electrical Tests

Analytical-grade chromium trioxide was calcined to temperatures of 500, 700, 1000, 1200, and 1400° C, respectively, in an atmosphere of argon; the experiments were repeated with oxygen. Two additional calcinations of laboratory-reagent-grade trioxide provided a comparison of four samples for the temperature of 1400° C.

The results for argon atmosphere showed p-type indication throughout; in oxygen, a p-type response was obtained up to and including 1000° C; n-type above. In the 1400° C comparison, both grades of oxide were p-type after argon treatment; after oxygen treatment, analytical-grade material was weakly n-type, whereas laboratory grade began with a slight n-type indication, but reverted to p-type. The 1400° C samples were all completely green after grinding, showing that alteration is not to be equated with $p \rightarrow n$ change (the possibility remains of a transitional change to n-type as part of the mechanism of cermet shrinkage).

The results on crushing of compacts are summarised in table III. The electrical and micrographic evidence, taken together, clearly shows that primary fracture in cermets occurs through altered oxide (grain-boundary) and subsequent fracture through unaltered oxide (transcrystalline). For plain oxide, the alteration present in the crushings and the fact that

TABLE II Properties of sintered "chromic oxide-0.25% carbon" compacts made from trioxide calcined in argon and oxygen.

Temperature of calcination (°C)	Shrinkage diameter (%)		Approximate alteration (%)		Chromium count	
	A	O_2	A	O_2	A	O_2
400	18.8	—	50	—	18	—
500	19.2	17.2	50	50	17	16
700	18.8	19.2	75	75	3	16
1000	17.2	16.0	75	75	5	9
1200	15.3	13.7	75	75	4	18
1400	15.4	5.6	75	50	21	>30*

*Difficult to compact; very dark green powder.

TABLE III Experiments on crushing of plain oxide and cermets.

Material and treatment	Semiconductor indication (mod. = moderate)	Alteration in microstructure (%)
Experiment 1		
(a) LG powder, as-received	mod. p	0
(b) As (a), pressed, sintered 1430° C in vacuo	mod. p	25
(c) As (b), refired	mod. p	25
(d) As (b), refired twice	mod. p	25
(e) As (b), refired thrice	mod. p	25
(f) As (e), crushed	mod. p	25
Experiment 2		
(a) LG Cr_2O_3 + $\frac{1}{2}$% carbon, sintered 1430° C	mod. p	25
(b) As (a), crushed to $\frac{1}{8}$ in.	mod. p	50
(c) As (a), crushed to $\frac{1}{16}$ in.	mod. p	50
(d) As (a), crushed $<$ 100 mesh (50% $<$ 350 mesh)	strong p	0
Experiment 3		
(a) LG CrO_3, calcined 1400° C in O_2	slight n	0
(b) As (a), pressed, sintered 1430° C in vacuo	mod. p	25
(c) As (b), but crushed	mod. p	50
Experiment 4		
(a) LG CrO_3, calcined 1400° C in O_2	slight n	0
(b) As (a), mixed with $\frac{1}{4}$% carbon, sintered 1430° C	mod. p	25
(c) As (b), but crushed 100 mesh (50% $<$ 350 mesh)	strong p	25

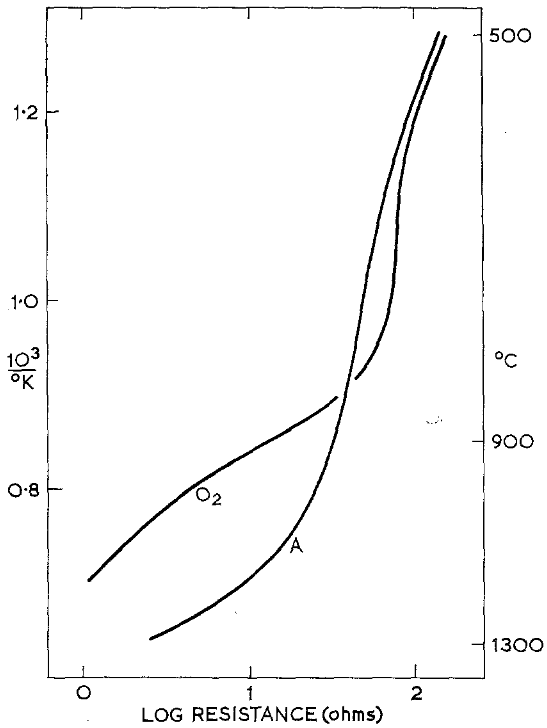

Figure 3 Surface p/n changes: plain oxide.

compacts crumble easily to a powder, consisting apparently of the original grains, suggest that fracture occurs in an intergranular manner only.

3.3. Surface p/n Changes

Two probes of platinum were embedded in a plain oxide compact during the pressing operation. The specimen was sintered normally (i.e. 1430° C, vacuum of 10^{-4} mm Hg). Subsequently it was heated in circuit with the resistance meter, first in argon (curve A, fig. 3), cooled, then reheated in oxygen (curve O_2). Note the reversion to p-type at approximately 850° C (near the temperature where lattice mobility increases significantly [11]). After the oxygen heating, resintering to 1430° C in vacuo or in oxygen gives rise to an n-type indication, thus completing a cycle. Similar specimens had an instantaneous response to oxygen in a standard 500° C p/n test; hence it is thought that the changes (fig. 3) refer predominantly to the surface between the probes. The form of curve A is generally similar to that given by other workers [12, 13, 20].

3.4. Conductivity along a Fracture

In many of the p/n tests, a particularly high response was often found at the first change from argon (used for heating up and stabilising) to oxygen, and the phenomenon appeared to be associated with fresh fractures. Consequently, a typical new cermet fracture was subjected to a conductivity/variable temperature test. Two platinum probes were strapped against the surface and the assemblage heated to 700° C, cooled, and reheated, in argon throughout. Serrations on a conductivity/temperature plot (presumably initiated by traces of oxygen in the argon) were prominent on first heating; were less noticeable on the first cooling; and were not subsequently observed. (Champion [21] has observed such instability in alumina.)

3.5. Chromium Trioxide Calcined at Low Temperatures

The higher oxides of metals (where they exist) are oxygen-deficient and the lower ones are oxygen-excess [22, 23]. The O/Me ratio at which an oxide may be said to be neutral in this respect varies, to a first approximation, with the extent to which higher oxides are stable. For chromium, one would expect the ratio to be amongst the highest. p/n neutrality in chromium oxides was briefly investigated by heating the trioxide from 20 to 450° C with probes in contact. The first indication, as the temperatures were raised and the trioxide decomposed, was clearly p-type. The resulting calcine was thought to be a mixture of Cr_2O_3 and CrO_2 [24-26].

4. Discussion

The results other than the electrical data may be briefly summarised as follows. The microscopic evidence suggests that a duplex structure is present, probably an intergranular network. The behaviour under crossed nicols suggests that the alteration gives a cubic structure. Chemical and X-ray analyses show that, on a gross scale, chromic oxide is not reduced to an intermediate oxide. Chemical analysis shows that chromic oxide is reduced principally to chromium, but a small discrepancy exists, consistent with either a shift in the O/Cr ratio of the whole matrix, or a larger localised shift of O/Cr ratio. No evidence for the presence of a metal network is given [3] by electrical continuity, hot-crushing, or acid-solubility tests, or by microprobe analysis.

The electrical results are consistent only with a sintering morphology in which the surfaces of the original particles of normal p-type oxide are modified. Further, a distinction must be made between sintering in oxidising conditions and sintering with reducing agents incorporated. Although it has been shown that the optical effect termed alteration is not synonymous with the semiconductor changes (the electrical tests will necessarily detect very slight changes in surface structure), it would seem likely that the change from p-type to neutral indication is a first stage in the formation of a discrete layer. If the heating takes place with reducing agent present, the surface of the particles is reduced in depth and, regardless of the nature of the shrinkage mechanism, the driving force would be augmented by the diminution in volume caused by transformation to metal or lower oxide. That the bulk of the particles remains p-type, in spite of both the reducing potential and temperatures adequate for lattice diffusion, is explained by the ability of chromium to take up a high-valency state. The probable sequence in oxidising conditions is quite different; though paradoxically the final structure is somewhat similar to that obtained in reducing conditions. It is thought that the behaviour is intimately related to the volatility of chromium trioxide [27, 28], and that such loss leads to the formation of a film of the same nature as in reducing conditions through hypothetical disproportionation reactions such as $Cr_2O_3 = CrO_3 + Cr$ or $5Cr_2O_3 = CrO_3 + 3Cr_3O_4$. The occurrence of vapour reactions would explain the absence of shrinkage in plain oxide compacts in oxidising conditions; in contrast, the shrinkage in reducing conditions is consistent with the occurrence of solid-state processes for matter transport, as a result of either one defect mechanism, or two or more mechanisms in series. Of possible mechanisms, the present work has established that particle surfaces may be changed from p-type to neutral, and also that an embryonic second phase may be found; some evidence has also been found for the existence of n-type oxide, which could profitably be substantiated by quenching experiments. In the time available, it was not possible to determine directly the constitution of the altered film. Evidence on sub-oxides [5, 29-36] and analogy with the Fe-Cr-O system [31-36] suggest that it might be Cr_3O_4.

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