A KINETIC STUDY OF THE ACTIVATED SINTERING OF CHROMIC OXIDE.

by

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ABSTRACT

High strengths and densities of carbon activated chromic oxide had been observed by Stone in a general study of the effect of admixed reducing agents, particularly carbon, on the sintering of chromic oxide.

The present work was undertaken to elucidate the mechanism, to which this enhanced sintering rate could be attributed.

A survey of the literature outlines present theories and mechanisms relevant to sintering processes, while solid and liquid state sintering have been discussed with their particular application and limitation to the present system.

Control of the dependant variables in the sintering process was utilised to define the mechanism of the activated sintering.

Confirmation of the diffusion coefficients obtained from this kinetic data was sought utilising tracer techniques in the case of the chromium ion diffusion in the oxide.
ACKNOWLEDGEMENTS

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The author is grateful to Professor L.W. Derry and Dr. R.L. Samuel for their support during the work.

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Comparison between Apparent Diffusivities and Cation Diffusivities as Deduced from Isothermal Data and Tracer Techniques Respectively in Carbon Activated Chromic Oxide

Schematic Representation of an Intermediate Step during the Activated Sintering of Chromic Oxide with Carbon
The present investigation was a consequence of work performed in the author's laboratory by Stone. His work had its origin in the production of high strength, high density cermets by novel means. Briefly, this consisted in the reduction in situ, of oxide powder compacts with the agency of an added reducing agent, the amount of which was controlled such that only a proportion of the oxide particle was reduced. The consequence of this was the production of a cermet of high strength by combining metallic and ceramic properties to the best advantage - the oxide particle being surrounded by, and interconnected with, a metal network.

As information on the sintering behaviour of partially reduced oxides increased, a complementary study of the mechanism of this sintering was indicated. For this study chromic oxide was chosen, while the added reducing agent was carbon. It is an investigation of the kinetic and mechanistic mode of the activated sintering of this oxide that is herein described.

From the outset, the work was considered with regard to a strict control of the dependent variables in the
sintering process. To this end, standardisation of procedure was maintained throughout the work; analyses of the oxide (chemical and size) were conducted and their significance considered. Kinetic data on the sintering of activated chromic oxide - standardised at \( \frac{1}{2} \) wt% carbon admixture - was compared with that of the plain oxide and comparable work on similar systems by other authors. Other variables such as atmosphere control, equilibrium partial pressure and particle strain have been dealt with, in a manner commensurate with their considered significance.

The theories of solid and liquid state sintering have been utilised to propose a hybrid model for the activated sintering of chromic oxide. Diffusion data obtained by the application of this model to the isothermal kinetic data, have been compared with diffusivities of the cationic species obtained by an independent tracer technique. The consequence of the cationic species being rate controlling in the activated sintering process is reconciled with the enhanced anionic mobilities in the activated state, together with the relevance of Hedvall's \(^{29,34}\) work on the increased reactivity of solids during incipient transformations.

An electron microscopical survey of the behaviour of activated and plain oxides is included. Though not in itself conclusive, it is complementary to the aforementioned work, and provides an interesting insight into the sintering
behaviour of the plain and activated oxides at comparable temperatures.
LITERATURE SURVEY

Although this work is concerned primarily with the mechanism and kinetics of sintering with the addition of an activating agent, a summary of general sintering theory is given. This is followed by the more specific conditions applicable to the work studied herein.

Sintering:

The term sintering is used to refer to that process whereby powders may be consolidated into dense polycrystalline aggregates by heating.

During sintering complementary changes occur. Depending on the degree of sintering, the mass of open pores, apparent in the green unsintered state, alter in such a way as to reduce the overall porosity.

Observations of sintering processes have established that the nature of the powder, pressing condition, impurities - indigenous or added, sintering time and temperature, and atmosphere may affect in varying degree the rate of sintering and the state of the final product.

In view of the diversity of variables that are significant in sintering, results of sintering studies are
frequently conflicting and difficult to elucidate in an unambiguous manner. Many theories have been proposed on model systems with the objective of quantitative analysis of the stages that occur in sintering. These have often been criticised for their abstraction. Their deductions and postulations must therefore be considered with a view to the systems to which they pertain. For example, seldom in powder compacts do particles approach the spherical shape and uniform size distribution of the ideal system. Even an imperfect model though allows one to study many of the changes occurring during sintering.

In studying the sintering kinetics of compacted powders it is usual to measure changes of linear or volume dimensions either singly or in combination as a function of controllable variables such as temperature and time of sintering, impurity levels, particle size and atmosphere.

General Theory:

In 1949, Kuczynski\(^1\) published his now classic paper on the determination of the transport mechanism in solid state sintering from the time laws of neck growth. In the interim, these laws have been applied to many systems and slightly modified by several authors. Essentially all these authors concluded that, for crystalline materials, the dominant transport mechanism in neck growth between two
Possible Flux Paths In Sintering Process.

1) Surface diffusion, surface source.

2) Volume diffusion, surface source.

3) Grain boundary diffusion, grain boundary source.

4) Volume diffusion, grain boundary source.
sintering spheres in contact is volume diffusion. This stems from the observation that the neck radius increases with a time exponent of approximately $\frac{1}{5}$ and that the activation energy for the sintering process approximates to that of bulk lattice diffusion.

For the other possible sintering modes considered by Kuczynski, namely viscous or plastic flow, evaporation and condensation and surface diffusion, time exponents for neck radii of $\frac{1}{2}$, $\frac{1}{3}$ and $\frac{1}{7}$ respectively for the first stage of sintering were suggested.

The second stage or closure of isolated pores has been less extensively investigated.

Coble$^2$ has analysed the possible sources and sinks for atoms that may contribute in the sintering process. The flux paths over which transport may occur are shown in Fig. 1.

These are:

1) From the sphere surface to the neck surface by surface migration
2) From the sphere surface to the neck surface by volume diffusion
3) From the grain boundary to the neck surface by grain boundary diffusion
4) From the grain boundary to the neck surface by volume diffusion.
A fifth possibility exists which would involve transport from the particle surface through the vapour to the neck. In the case of most metals this is ignored because of their relatively low vapour pressures; but this mode of transport has been found important in the sintering of NaCl$^3$ and Cr$_2$O$_3^4$.

Mechanisms of transport involving means other than diffusion have been considered by Kuczynski (1949)$^1$.

**Plastic Flow:**

The subject of mass transport into the neck by plastic flow due to dislocation motion has also been recently considered by Lenel, Ansell, Salkind and Early$^5$. These authors studied the stress dependence of the rate of sintering in compacts and concluded that dislocation flow is the rate controlling process in sintering under zero external load. Their conclusions are open to doubt for the following reasons:

1) Kuczynski has shown that, since the strain rate in flow theories is proportional to stress, a $t^{\frac{1}{2}}$ relationship should be observed in neck growth if plastic flow is the dominant transport mechanism. This has never been observed in crystalline systems (glass spheres sintering on to flat glass observe this law).

2) There exists no experimental data or analysis of the resulting state of stress within the neck for crystalline sintered systems.
3) It is difficult to conceive of volume stresses large enough to cause dislocation, multiplication and pile up for:

\[ x = \frac{\text{neck radius}}{a} > 0.1 \]

Surface Diffusion:

As a final step in his formulation of the theoretical rate law for surface diffusion Kuczynski had to integrate the form \( \frac{dx}{dt} = \frac{B}{\rho^3} \), where \( \rho \) = radius of curvature of neck, and B a constant. He assumed \( \rho = \frac{x^2}{2a} \) when \( \frac{x^7}{a^3} = kt \)

Nichols and Mullins \(^6\), though, have recently applied a more rigorous analysis for spheres sintering by a process of surface transport and have found that the time exponent varies from \( \frac{1}{5.9} \) to \( \frac{1}{6.6} \) for \( 0.1 < x/a < 0.4 \) (which is the usual sintering range). They showed quite rigorously that the time exponent for surface diffusion lay nearer \( \frac{1}{6} \) than \( \frac{1}{7} \) - similarly by inference, the volume diffusion time exponent should be about \( \frac{1}{4} \) rather than \( \frac{1}{5} \).

Vapour transport:

An equation leading to the relation of the equilibrium vapour pressure over a curved surface to the radius of curvature \( \rho \) of that surface was first derived by Lord Kelvin \(^8\).
\[ \frac{\Delta p}{p_0} = -\gamma V_0/RT_p \]

where \( p_0 \) is the equilibrium vapour pressure over a planar surface, \( \Delta p \) the decrease in vapour pressure over the curved concave neck surface, \( \gamma \) the surface tension of the solid, \( V_0 \) the molar volume and \( T \) the temperature. By inserting the expression for \( \Delta p \) into the Langmuir\(^7\) adsorption isotherm, Kuczynski obtained

\[ \frac{K}{a^3} = \frac{3\pi M}{2\pi R} \left( \frac{M/2\pi RT}{d^2RT} \right)^{1/2} p_0 \]

(where \( M \) = molecular weight and \( d \) = density),

the time exponent for neck radius increase therefore being \( \frac{1}{3} \) for an evaporation-condensation vapour transport mechanism. This mechanism is expected to operate during sintering of particles of material having high vapour pressures such as zinc or cadmium. Good verification has been obtained of the \( t^{3} \) law for the sintering of NaCl spheres\(^3\), (also Cr\(_2\)O\(_3\))\(^4\).

**Motivation:**

1) Neck growth during sintering results in a decrease of free surface and consequently in the total surface free energy of the system. This has long been recognised as a motivating force for sintering. Though this excess surface energy is never very great, there exist in the neck vicinity, stresses large enough to produce the changes observed during sintering. Kuczynski derived to a first approximation, the relation \( \sigma = -\gamma/\rho \) where \( \sigma \) is the stress acting on the neck.
surface, γ the surface tension and ρ the radius of curvature of the neck region. This stress is tensional and acting outwards. It is this stress in the neck that may induce mass flow.

2) By considering the voidage around the particles as a vacancy fluid, the neck cavity can be considered as a convexity into which the vacancies will evaporate. Consequently the vacancy pressure in the neck area will be greater than under a flat surface in compliance with $\Delta P_o = -\gamma V_o/RT_o$

Since vacancy pressure is proportional to vacancy concentration, then $\Delta C / C_o = \gamma V_o / RT_o$ where $\Delta C$ is the excess vacancy concentration in the neck, and $C_o$ the equilibrium concentration under a planar surface. Thus where there exists a concavity there is a potentially favourable flux path for vacancies and consequently mass transfer in the complementary direction. The excess vacancies have to be removed from the system by depositing them either on a nearby surface or in the grain boundaries. The high mobility of grain boundaries can expedite this removal, or if sufficiently fluid, collapse and absorb the vacancies completely. Overall shrinkage can then result. This, however, is not the case if vacancies are eliminated on a free surface. Here a change in particle shape is possible but not a centre to centre approach.
Constants used with various sintering models.

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<tr>
<td></td>
<td>K</td>
<td>m</td>
</tr>
<tr>
<td>2</td>
<td>(2)</td>
<td>0.50</td>
</tr>
<tr>
<td>2</td>
<td>(20/2^{1/2})</td>
<td>0.40</td>
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<tr>
<td>68</td>
<td>(31/\pi^2)</td>
<td>0.46</td>
</tr>
<tr>
<td>68</td>
<td>(15\delta)</td>
<td>0.33</td>
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<tr>
<td></td>
<td>(50b/7\pi)</td>
<td>0.31</td>
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where \(\delta\) represents the cube root of vacancy volume & \(b\) represents grain boundary width.
A mass flux may be manifested by surface or volume diffusion (or in the particular case vapour transport); it is this mass diffusion mechanism that is considered to be the most important in sintering phenomena.

The characteristic equation derived by Kuczynski\(^9\) for volume diffusion was

\[
x^5/a^2 = \left(\frac{K\gamma}{RT}\right) D_v t,
\]

where \(D_v\) = volume self-diffusion coefficient.

Experiments on the sintering of copper wire\(^9\) (also silver) to a cylinder yielded self-diffusion coefficients, utilising the above equation for \(D_v\), that were in good agreement with those obtained by tracer techniques.

Although differing slightly in form, the sintering models of Coble\(^2\), Kingery and Berg\(^3\) et al, based on a volume diffusion mechanism, all resolve into an equation of the form,

\[
\frac{\Delta l}{l_0} = \left(\frac{K D_v \gamma \delta^3 t}{r^3 kT}\right)^m,
\]

where \(\Delta l / l_0\) is the dependent variable being linear fractional shrinkage, \(r\) the mean particle diameter, while \(K\) and \(m\) are numerical constants peculiar to each model. For models based upon grain boundary diffusion (Coble, Johnson and Culter) the parameters are related:

\[
\frac{\Delta l}{l_0} = \left(\frac{K D_B \cdot b \cdot \gamma \cdot \delta^3 t}{r^4 kT}\right)^m,
\]

where \(D_B\) is the grain boundary diffusion coefficient and \(b\) the grain boundary width.

The values for the constants \(K\) and \(m\) are shown in Fig.2.
Johnson and Clark\textsuperscript{10} proposed a sintering model in which both grain boundary and volume diffusion occurred concurrently. The linear shrinkage was then related accordingly to both volume and grain boundary diffusion coefficients.

Recently, experiments on the sintering of alumina spheres\textsuperscript{11} have demonstrated that this oxide sinters by a volume diffusion process. The rate of sintering, however, was found to be greatly dependent on the ambient atmosphere. In atmospheres of high oxygen potential, the apparent energy of activation of the process, 150 kcal/mole agreed closely with the value for anion self-diffusion in alumina\textsuperscript{12}. The coefficient of self-diffusion of the oxygen ion, though, as obtained from neck growth rate measurements appeared to increase greatly with the oxygen potential of the sintering atmosphere. In a reducing atmosphere of pure hydrogen sintering is extremely rapid. The activation energy for this process was found to be around 200 kcal/mole. The sintering rate is controlled by the rate determining partial process, that is, the slowest diffusion mechanism occurring in the solid (assuming the sintering to be diffusion dependent).

As the activation energy obtained from the experiments performed in an oxidising atmosphere is the same as that for oxygen ion diffusion, it should be concluded that the anion
is the slowest diffusing species and therefore process controlling. The observation that the oxygen diffusion coefficient increases with oxygen partial pressure in the atmosphere may be indicative that an interstitial diffusion mechanism is operative and that there are few oxygen vacancies. The change of activation energy in a reducing atmosphere may be explained by a change of diffusion mechanism. It is possible that suboxides are formed (hydrogen at high temperatures is capable of reducing alumina to lower oxides such as AlO and Al₂O with the possible creation of oxygen vacancy sites). Thus in a strongly reducing atmosphere the diffusion of oxygen ions may become oxygen vacancy diffusion.

During the initial stages of sintering a high shrinkage rate has sometimes been observed at low shrinkage values. This has been observed by Coble in the initial sintering of Al₂O₃ and Fe₂O₃, and attributed to shrinkage of individual grains, an accessory sintering mechanism, or to the non-isothermal shrinkage which occurs while the samples equilibriate with the ambient furnace temperature.

The diffusion of iron and oxygen in Fe₂O₃ has been considered by Himmel, Mehl and Birchenall. They deduced that oxygen diffuses faster than iron in Fe₂O₃ since measured rates of oxidation of Fe₃O₄ to Fe₂O₃ are faster than predicted from iron self-diffusion. In the sintering of
Fe$_2$O$_3$ the diffusion of the slower diffusing species (Fe) is expected to be rate controlling in sintering, if bulk diffusion is the predominant sintering mechanism. Coble, in the initial sintering of Al$_2$O$_3$ and Fe$_2$O$_3$, compared measured diffusion coefficients of Fe in Fe$_2$O$_3$ with those calculated from sintering rates. Good agreement was obtained with the tracer work of Lindner and that of Himmel. It was observed that the temperature dependence of sintering of Fe$_2$O$_3$ was equal to that of iron self-diffusion in Fe$_2$O$_3$, the agreement between extrapolated and calculated diffusion coefficients substantiating Kingery and Berg's sintering model.

**Grain Growth:**

For the achievement of maximum density at the most rapid rates grain growth must be inhibited during sintering operations, in view of the marked particle size effect on sintering rate. Burke has indicated that in relatively pure materials, the porosity initially present inhibits grain growth, and, when the porosity is reduced to a critical value, exaggerated grain growth occurs. Residual porosity, trapped within the grain, is then more difficult to eliminate by a diffusion flux. Firstly the diffusion paths are longer and the flux is therefore decreased; secondly the gas from the ambient atmosphere must diffuse out of the closed pores. That this gaseous diffusion may become the slowest partial process
and therefore rate controlling was demonstrated by Rhines\textsuperscript{11,2} in the sintering of copper. Knowledge of the chemical diffusion coefficients of gases, the pressure variation of their solubilities, and self-diffusion coefficients of the solid is required to predict which gases in a particular system become, or could become, rate controlling during the later closed-pore stage of sintering.

\textbf{Atmosphere:}

The effect of ambient atmosphere on the initial stages of sintering was interpreted for a diffusion mechanism in terms of known or implied defect structures by Marshall\textsuperscript{16} and Gray\textsuperscript{17}. Thus, for Al\textsubscript{2}O\textsubscript{3} more rapid sintering in reducing or neutral atmospheres (as previously mentioned) may be taken as evidence for slower diffusion of oxygen than aluminium ions, since an increase in oxygen vacancy concentration in neutral or reducing atmospheres would increase the apparent diffusion coefficient of oxygen.

\textbf{Impurities:}

The fact that a bulk diffusion mechanism is operative in sintering does not immediately lead to a complete understanding of the effects of impurities on sintering rates. For sintering to be single phase the impurity additive must be present in such quantity that its solid solubility limit is not exceeded.
Alumina is a case that may be taken by way of example. The addition of either alkaline earth oxides or aluminium fluoride to alumina inhibits sintering. The conditions under which this would obtain are such that the impurity M\(^{2+}\) would tend to inhibit diffusion and sintering if the aluminium ions were the slower diffusing species; the M\(^{2+}\) being here distributed to fill Al\(^{3+}\) vacancies. This explanation may, however, be quantitatively rejected since one third of the aluminium sites are initially vacant, the observed effect being at least an order of magnitude larger than the vacancy concentration change. Similarly, inhibition by the fluoride would imply that the oxygen was the slower-diffusing ion. These conflicting conclusions may be rationalised by assuming that for either or both observations a) a reduction of surface energy is the principal effect b) impurity - vacancy coupling is occurring or c) a Kirkendall effect is operative.

Since bulk diffusion is of great importance in sintering, the effect of additive impurity on grain growth and size must be considered. Within the limits of solid solubility, different solubilities of the grain boundaries would require the solute gradient to be diffused with the moving boundary. Migration of the grain boundary would then exhibit kinetics typical of bulk rather than boundary processes. If additives
are in excess of the solubility limit, the effect of grain growth will depend upon the distribution of the second phase. The most effective distribution for grain growth inhibition would be a continuous grain boundary film; less effective, a highly dispersed second phase.

Grain boundary effects usually have a great influence upon the properties of ceramics. It was stated by Smothers and Reynolds\textsuperscript{18} that the presence of a glass phase at the boundaries inhibits grain growth. Coble\textsuperscript{19} observed that discontinuous grain growth in alumina was inhibited by the presence of a small percentage of magnesia, thus making possible the production of very high density sintered bodies. Navias\textsuperscript{20} showed that, in the same binary system of MgO and Al\textsubscript{2}O\textsubscript{3}, an increased rate of spinel formation occurred in hydrogen, in contrast with vacuum, and that this was due to the formation of a complete surface layer of MgO on the alumina due to vapour transport. In an oxidising atmosphere the magnesia does not vaporise and reaction only occurs at direct contact points.

**Particle Surface:**

Recent experiments in sintering indicate that surface diffusion can play a dominant role in neck growth. The work on alumina by Oishy and Kingery\textsuperscript{12} indicates that this is
true for many oxides. Additionally the work of Wilson and Shewmon indicates that surface diffusion can play a dominant role in neck growth during the initial sintering of copper spheres. This paper stresses, in the light of the importance of surface diffusion processes, the surface condition of the sintering particles. It emphasises the association between variables affecting surface diffusion and concurrent sintering, i.e. surface cleanliness, atmosphere and surface active materials. They showed from available data and analyses that surface diffusion should control material transport in the neck growth stage of the sintering of copper spheres. Also they indicated that transport along grain boundaries may be expected to contribute substantially to neck growth beneath some critical temperature of about 0.70 TM.

Surface films may be beneficial during a sintering process if they provide a chemically active surface of higher mobility and surface energy than the basic particle. This type of sintering is exemplified in the "activated" sintering of ceramics and metals. Such use of activating agents as halides has been considered by Eudier. Enhanced chemical activity, diffusion rate and vapour transport were the effects of thin oxide films of the order of 500 Å on sintering of metal powder compacts studied by Ramakrishnan and Tendolkar.
When studying the sintering of copper particle compacts, Calow and Tottle\textsuperscript{24} found the temperature of maximum shrinkage rate to be about 300°C higher in oxygen as compared with a reducing atmosphere of hydrogen. They attributed this to the differences in degree of dissociation of the oxide film as it affected the production of active surfaces for diffusion and sintering processes. Williams, Jones and Westmacott\textsuperscript{25} observed the effect of oxide surfaces on the sintering of uranium. The stable oxide is normally the dioxide; a layer of the monoxide was found in certain conditions and tended to increase with time and temperature. The apparent changes in pore shape and oxidation rate led to the belief that the behaviour of the monoxide film was significant in determining the sintering mode of the powder. Williams et al\textsuperscript{25} stated that during the sintering of a metal in which a surface oxide film was present, an increase in the available free energy of the system or net driving force for sintering could be achieved if either or both of the two interfacial energies could be increased. Sintering would also be enhanced if the intrinsic mode of sintering of the oxide film itself could be improved.

The bonding behaviour of metals to uranium dioxide was studied by Milner\textsuperscript{26}. The wetting of the oxide improved when the energy $\gamma_{SL}$ of the liquid-solid interface decreased. High values of $\gamma_{SL}$ appeared to be typical of molten metal -
refractory oxide systems and are attributable to the peculiar structure of high energy oxide surfaces which are believed to be dominated by oxygen anions\textsuperscript{27,28}.

**Reactivity:**

Lattice imperfections at or near the surface of crystalline materials often play a predominant part in determining the properties of the solid. Chemically identical solids may differ in properties owing to differences in grain size, i.e. high disorder prevalent at the grain boundaries. In ionic crystals the predominant binding force is between ions of opposite polarity. Owing to unbalanced electrostatic forces at the surface, polar groups in the vicinity may be attracted to active sites. Ions at or near edges are presented with more favourable reaction possibilities. "Fresh" crystal facets relatively free of adsorbed molecules are particularly likely to attract an adsorbed film. This film will eventually affect the surface properties of a comminuted solid such as a milled oxide powder. The state of minimum energy in any solid is in general that of perfect crystallinity. The presence of grain boundaries and other lattice defects increase the energy content. So-called "active" solids possess measurably greater heat of solution than inactive samples of the same material (an indication of the energy associated with the state). Solids with discontinuities are therefore unstable relative to the perfect lattice. These
discontinuities will tend to disappear if the units in the lattice have the necessary mobility. Therefore discontinuities will persist at low temperatures and tend to be removed by heating, i.e. grain growth. Also, the formation of a solid by a chemical reaction usually results in an ill developed lattice. In this condition a solid can exhibit unusually high reactivity.

Active solids formed by dehydration of hydrated metal oxides were studied by Fricke. Active solids also occur in the early stages of reaction between two or more solid materials in intimate mixture. There, activity is associated with the incipient destruction of the stable crystal lattice and not with the incompleteness of the reaction. The principal conclusion reached by Fricke, Huttig and Hedvall was that a solid product of a chemical change, or a solid in a state of incipient reaction with some admixed reagent, may possess abnormally high activity at its surface. Brindley has reviewed the effects of calcination on crystallographic structure. Ultrafine particles of oxides produced at low calcining temperatures, exhibit subsequently high sintering rates and reactivities. In many instances the structure of the calcined oxide bore a resemblance to the parent salt (Iwase). In a series of experiments with zinc oxide under reduced partial pressures of oxygen, Gray observed the rapid diffusion of zinc, such that a metal coating was
formed upon the particles. He showed that a high surface
defect concentration could exist and that this was closely
related to the phenomenon of sintering. He observed
abnormally high vapour pressures and deduced that this was
evidence of surface modification. This does not necessarily
imply that a defect type structure has enhanced sintering
properties. The effect of varying oxygen partial pressure
on the diffusion rates of zinc in zinc oxide from different
sources was studied by Roberts. He found that there was
an increase in some cases and a decrease in others. In
certain cases the shrinkage was enhanced although the ambient
oxygen partial pressure was such as to drive the oxide
towards stoichiometry.

It is established that the sintering behaviour of
uranium dioxide is affected to a marked extent by its oxygen
content; the ambient oxygen pressure was shown by
Williams to affect the sintering mode in consequence of
its effect upon the oxygen - uranium proportionation. They
confirmed that reducing hydrogen atmospheres driving the
normally non-stoichiometric uranium dioxide towards
stoichiometry decreased the rate of densification of the
oxide. The shrinkage rate in neutral atmospheres was found
to be determined predominantly by the original oxygen-
uranium ratio in the oxide.
It has been indicated that departure from stoichiometry has often been conducive in promoting the intrinsic lattice mobility and hence sintering rate. Moorthy and Rac\textsuperscript{38} found that a hydrogen atmosphere was beneficial to the sintering process, and implied that the pertinent variables are physical in form – such as distribution of particle size.

**Role of Trace Impurities:**

Atomic diffusion processes in solids may depend upon trace impurities. Many diffusion processes proceed in solids by a vacancy mechanism, the diffusive jump occurring only when there happens to be a vacancy in an adjacent lattice site. It is seen that the rate of diffusion in such cases will depend upon the vacancy density in the crystal. These arise in two ways, firstly, from thermal disorder in any crystal, the defect density at any temperature having been formulated by Frenkel, Schottky and Wagner\textsuperscript{39}; secondly, from the presence of foreign impurities which in compounds can produce vacancies in order to maintain a charge balance. Thus, if Cd\textsuperscript{2+} is added to NaCl, a vacancy appears on a cation site. Self-diffusion of Na\textsuperscript{+} in such a crystal depends upon the number of cation vacancies, hence the presence of Cd\textsuperscript{2+} increases this diffusion rate (and also the electrical conductivity which results from ionic motions in the case of NaCl).
It is apparent that so long as the concentration of impurities which produce vacancies in this way is at least comparable with intrinsic thermal disorder, the impurity effects will be important or dominate the diffusion process. Typical vacancy concentrations produced by thermal disorder (at temperatures which are significant in diffusion studies) may be 100 ppm or less.

As previously indicated, the source of ZnO used significantly affected the densification rate. This was because of variations in impurity content of the oxide (and possible particle size effects). Studies on the reactivity of MgO by Coble and Burke showed that the vacancy concentration and consequently the reactivity was controlled by impurities. Since compounds which are used in sintering processes are seldom pure, it will often transpire that impurities will predominate over the intrinsic vacancy concentrations, which might fall into the range 0.1 to 0.001% at normal sintering temperatures. It seems that the impurities most effective in promoting the sintering rate will be those of higher valency which affect the important vacancy concentration; it is cation diffusion rate determining and hence cation vacancies that are important in Fe$_2$O$_3$, while it is the anion diffusion and anion vacancies that dominate the sintering process in the case of Al$_2$O$_3$. 
In accordance with Gibbs' theorem, the surface layer of a particle will not necessarily have the same composition as the bulk. It is for this reason that a solid of ostensibly low impurity content may have prevalent at its surface an effectively high impurity level, with the attendant properties already mentioned. Consequently, this heterogeneous distribution will have a greater effect on the particle surface mobility.

**Constitutional Effects:**

Keiffer suggested that in most technically pure powders even with purities of 99.95%, there exist during sintering eutectic films with the impurities, so that in practice sintering rarely takes place with the total absence of a liquid phase. Even pure wire specimens at 0.81-0.91 Tm exhibit so pronounced a mobility of the outermost atomic layers that it appears justified to speak of a liquid surface film. Depending upon the impurity elements present, the "alloy" layer may promote surface diffusion and therefore have some effect upon low temperature sintering.

**Carbon Admixtures, and Impurities in Chromic Oxide:**

The stoichiometric proportion of carbon required for the complete reduction of chromic oxide is 19.2 wt%. According to Boericke the reduction of this oxide by carbon proceeds, after the initial reduction, via the
intermediary of the carbide,
\[ \text{Cr}_2\text{C}_6 + 2\text{Cr}_2\text{O}_3 = 27\text{Cr} + 6\text{CO} \]

It is reasonable to conceive that at the oxide surface there exists a highly defect layer consisting of mutually dissolved or co-existing oxide, carbide, carbon and trace impurities. Experimental evidence\(^4^4\) suggests that chromic oxide is very slightly soluble in chromium, and vice-versa, and that at 80 wt% chromic oxide an eutectic occurs at 1660°C. The effect of dissolved oxygen in the chromium is to lower considerably its melting point.

At the melting point of chromium the standard free energy\(^4^5\) of formation of chromic oxide has been found to be 90,000 cal/mole \(O_2\). Equilibrium calculations show that at 1000°C the partial pressure of oxygen over chromium and chromic oxide is \(10^{-25}\) atmospheres. Chromium should therefore be capable of extracting oxygen from any source where the oxygen potential is greater than \(10^{-25}\) atmospheres. It has been confirmed by Gulbransen and Andrew\(^4^6\) that decarburised chromium oxidises rapidly on heating to only 800°C at pressures of \(10^{-6}\) mm Hg.

Though the solubility of carbon in chromium\(^4^4\) is small (if any) the effect of higher carbon contents on chromium is pronounced. Stable carbides of chromium
Cr$_{23}$C$_6$, Cr$_7$C$_3$ and Cr$_3$C$_2$ have been investigated and identified at 5.88, 9 and 13 wt% carbon respectively. At 13 atomic percent carbon an eutectic occurs between chromium and the carbide Cr$_{23}$C$_6$. This eutectic has an invariant temperature reported to be as low as $1485^\circ$C. The constitutional effect therefore of carbon is to reduce the temperature at which liquid may exist, when it is localised to that part of the sintering system where there exists carbon, as carbide, and chromium in the requisite proportion.

Of the impurities that are present in this oxide, silicon ranks most prominently (as indicated by the mass spectrometric analysis). At 12 wt percent silicon an eutectic occurs between chromium and Cr$_3$Si, the temperature being reported as $1515^\circ$C. At high silicon concentrations (viz 75 wt%) a low temperature eutectic exists between the intermetallic compound CrSi$_2$ and silicon - the temperature being at $1320^\circ$C. This high silicon content was considered significant in the sintering of chromic oxide whose fractionation was effected utilising sodium silicate surfactant as a dispersing agent. Within the impurity range found, sulphur could have a constitutional effect upon the melting point of chromium. At 2.2 wt% of sulphur a monotectic occurs whose invariant temperature is $1550^\circ$C.
Thus it is seen that by reference to but a few of the trace impurities and controlled admixed reagents, it is possible to produce a localised constitutional effect, especially significant at oxide particle surfaces, where impurities may be derived from within and without the particle.

These arguments together with the aforementioned ones concerning the effect of impurities on the defect solid state, lead one to consider during sintering, not an ideal solid but one in which there could exist as a consequence, a state of high mobility. For these reasons the sintering of chromic oxide with admixed carbon must also be considered, perhaps in over-simplification, from the point of view of liquid phase sintering.

Liquid Phase Sintering:

Densification, by sintering in the presence of a liquid phase - which markedly accelerates the shrinkage rate - has received but little attention from the point of view of developing quantitative relationships between process variables. Kingery\textsuperscript{52} considered on a quantitative basis the sintering of a major solid phase in conjunction with a liquid which completely wetted it, and in which the solid was partially soluble. Lenel\textsuperscript{53}, Curland and Norton\textsuperscript{54},
and Conuon and Lenel\textsuperscript{55} agreed that for complete densification, 1) an appreciable amount of liquid, 2) an appreciable solubility of the solid, and 3) complete wetting are requirements during liquid phase sintering. Three steps are identifiable a) liquid phase formation and particle rearrangement, b) increase of density by solution and reprecipitation of the solid and in some cases c) a slowing of densification by the formation of a solid skeleton.

The driving force for liquid phase densification can be best interpreted in terms of surface energies. If

\[
\gamma_{SV} > \gamma_{LV} > \gamma_{SS} > 2 \cdot \gamma_{SL}
\]

Where \(\gamma_{SV}\) = surface-vapour tension  
\(\gamma_{LV}\) = liquid-vapour tension  
\(\gamma_{SS}\) = solid-solid tension  
\(\gamma_{SL}\) = solid-liquid tension

then complete grain penetration occurs\textsuperscript{57}. Interparticle pores are formed in the liquid phase, the decrease in this liquid-vapour pore surface area and concurrently the net overall free surface energy providing the driving force for densification in the system.

Kingery\textsuperscript{52} found that in the initial rearrangement process the shrinkage \(\Delta l/l_0\) was proportional to \(t^{1+y}\), where \(1+y\) was somewhat larger than unity.
During the solution precipitation process for spheroidal particles he correlated the linear shrinkage and process variables. Initial rates of densification during this period may be controlled either by the rate of diffusion of material from the particle contact area or by the rate of phase boundary reaction. Diffusion rate controlling:

\[
\frac{\Delta l}{l_0} = \left[ \frac{6k_2^6Dc_0 \gamma_{LV} \cdot V_0}{k_1^2 RT} \right]^{\frac{1}{3}} \cdot r^{\frac{4}{3}} \cdot t^{\frac{1}{3}}
\]

and for phase boundary reaction rate controlling:

\[
\frac{\Delta l}{l_0} = \left[ \frac{2k_3^2k_2 \cdot \gamma_{LV} \cdot c_0 \cdot V_0}{k_1^2 RT} \right]^{\frac{1}{2}} \cdot r^{-1} \cdot t^{\frac{1}{2}}
\]

where \(k_1, k_2, \text{ and } k_3\) are constants; \(\delta\) the boundary thickness, \(c_0\) the solubility of solid in liquid, and \(V_0\) the molar volume.

A continuation of Kingery's work showed that experimental determination of shrinkage rates could be used to distinguish between the rate controlling steps. The annotation of the effect of control variables on shrinkage is summarised by Brophy, Shepard and Wulff in the nickel activated sintering of tungsten. Taking the general equation:

\[
\frac{\Delta l}{l_0} = \left( \frac{k c_0 \gamma_{LV} V_0}{RT} \right)^{l} \left( D_v \right)^{m} \left( C_A \right)^{n} \left( r_2 \right)^{p} \left( r_1 \right)^{q} \left( t \right)^{s}
\]
<table>
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<th>Rate-controlling step</th>
<th>l</th>
<th>m</th>
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<th>p</th>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>$\frac{1}{2}$</td>
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<tr>
<td>Matrix diffusion</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$-\frac{1}{2}$</td>
<td>$-\frac{1}{2}$</td>
<td>-1</td>
<td>$\frac{1}{2}$</td>
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<tr>
<td>a) Radially at flats</td>
<td>$\frac{1}{3}$</td>
<td>$\frac{1}{3}$</td>
<td>$\frac{1}{3}$</td>
<td>$\frac{1}{3}$</td>
<td>$-\frac{4}{3}$</td>
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</tr>
<tr>
<td>b) Circumferentially in surface layer</td>
<td>$\frac{1}{3}$</td>
<td>$\frac{1}{3}$</td>
<td>0</td>
<td>0</td>
<td>$-\frac{4}{3}$</td>
<td>$\frac{1}{3}$</td>
</tr>
<tr>
<td>c) Circumferentially in phase boundary</td>
<td>$\frac{1}{3}$</td>
<td>$\frac{1}{3}$</td>
<td>0</td>
<td>0</td>
<td>$-\frac{4}{3}$</td>
<td>$\frac{1}{3}$</td>
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<tr>
<td>d) Radially over entire sphere</td>
<td>$\frac{1}{3}$</td>
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<td>0</td>
<td>-1</td>
<td>$\frac{1}{3}$</td>
</tr>
</tbody>
</table>

in the general equation

$$\Delta t = (kC_0 \gamma \lambda V_0 / \kappa R T) \frac{1}{l} \cdot (D_v)^m \cdot (C_A)^n \cdot (r_2)^p \cdot (r_1)^q \cdot (t)^s$$

Fig 3
the exponents were correlated according to the rate controlling step as shown opposite in Fig.3, where the terms are as used hitherto, ($C_A$ is the overall concentration of surface activator to solid).

During the final stage of coalescence, it is to be expected that complete grain penetration cannot occur, since the material along a line between particle centres will all be solid. Consequently rapid densification corresponding to liquid phase processes are stopped. The densification rate should then decrease to that commensurate with solid state sintering under similar conditions.

Kothari and Waring, investigating the sintering kinetics of iron-copper alloys, with and without a liquid phase present, observed that above the melting point of copper, apparent diffusion rates increased by three orders of magnitude with an attendant lowering of activation energy. They concluded that although the apparent activation energies were lowered to about 0.7 of the value for solid state volume diffusion, the value was still too high to be consistent with diffusion in the liquid state (activation energy <10 kcal/mole).
Sintering with Specific Reference to Chromic Oxide:

The reduction in vacuo of chromic oxide by carbon has been studied by Baukloh and Henke\textsuperscript{59}, and the kinetics of hydrogen reduction of chromic oxide were studied by Strater and Mentell\textsuperscript{60}. Kramers and Smith\textsuperscript{61} considered Cr and Cr$_2$O$_3$ mixtures. The kinetics of reduction of oxides (alumina, thoria, beryllia and titania) with carbon were observed by means of carbon monoxide evolution by Komarek, Coucoulas and Klinger\textsuperscript{62}. The oxide shrinkages however were not studied. Clark and White\textsuperscript{36} reported that chromic oxide fired at 1550°C undergoes a shrinkage followed by an expansion; the changes were however, an order of magnitude less than those observed in the present work. Spriggs, Brisset, Rosetti and Vasilos\textsuperscript{63} were able to manufacture theoretical density chromic oxide by hot pressing at temperatures and pressures of 1150°C and 20,000 p.s.i. respectively. A large porosity reduction in the sintering of chromic oxide in vacuo or neutral atmosphere was found by Budnikov and Tresvyatsky\textsuperscript{64}. Stone\textsuperscript{65} found that small additions of reducing agents to chromic oxide resulted in a greatly enhanced sintering rate.

There appears to have been little work conducted on the sintering mechanism of chromic oxide either with or
without an added activating agent (as investigated by Stone$^{65}$). Barrett et al.$^4$ investigated the mechanism of sintering over the temperature range 500°C to 1700°C. By utilising the modulus of rupture as a criterion they deduced that above 1000°C there was a change in sintering mechanism to vapour phase diffusion. The process which obtained between 500°C and 1000°C was probably one of surface diffusion.

Stone$^{66}$ found that the shrinkage of carbon activated chromic oxide was independent of activating agent concentration over the range of $\frac{1}{4}$ to 10 wt % carbon admixture. He found the production of high density and hardness possible in chromic oxide (activated) that had been sintered to moderate temperatures only (0.73 $T_m$) for times of the order of 15 minutes. Chemical analysis of reacted chromic oxide - carbon compacts indicated that a slight reduction of oxygen content in the matrix occurred. It was concluded that modification of the oxide particle surface occurred during reduction, and that this entailed a change to a lower oxide or oxides and/or metallic chromium, although transient formation of an oxygen deficient layer of sub-stoichiometric oxide is implied (the oxide core remains unchanged, i.e. oxygen excess).
Hagel et al., used $\text{Cr}_2\text{O}_3$ in a determination of initial sintering kinetics. A study of the sintering of this material, in view of the large difference in component ionic diffusivities, should indicate unequivocally which ion species is rate controlling. Using three analyses by Kingery and Berg$^3$, Coble$^2$, and Johnson and Cutler$^6$ they concluded that the "model" diffusion coefficients were consistent with oxygen ion diffusion ($\text{O}^{2-}$ being the slower diffusing ion). Hagel et al. concluded that the initial sintering of $\text{Cr}_2\text{O}_3$ between 1050°C and 1300°C, could be best described as a volume diffusion dependent process in which the anions were the rate controlling species. They also considered that though a small particle size was used (0.280 $\mu$) a relatively large grain boundary area did not appear to help significantly mass transport during sintering.

**Determination of Ionic Diffusivities by Means of Radioactive Tracer Techniques:**

Values for ion diffusion coefficients in chromic oxide - both anionic and cationic - have been ascertained, utilising tracer techniques and diffusion sintering models, as previously mentioned. Hagel et al.$^6$, applying Coble's analysis, obtained for the anionic diffusion in sintered chromic oxide a dependence:

$$D = 67.4 \exp \left( -\frac{101,600}{RT} \right)$$
Utilising oxygen -18 exchange between gaseous oxygen and oxidised chromic oxide spheres Hagel obtained, for anion diffusivity, the conformity:

\[ D_{O,18}^0 = 15.9 \exp\left(-\frac{101,000}{RT}\right). \]

Order of magnitude agreement is here acceptable for the frequency factor \( D_0 \), considering the many assumptions required in applying initial stage sintering models.

Complementary work on cation diffusion in chromic oxide was also conducted by Hagel and Seybolt, using sectioning tracer techniques. They found that the diffusion of chromium ions in hot-pressed nitrogen equilibrated chromic oxide conformed to:

\[ D = 0.137 \exp\left(-\frac{61,100}{RT}\right) \]

for three different impurity levels. Oxygen partial pressure variation, and trace quantities of added CeO$_2$ and Y$_2$O$_3$ caused no significant change in this Arrhenius type dependence. A similar technique was used by Hagel for the investigation of self-diffusion in polycrystalline chromium. The resulting dependence of self-diffusion coefficient of chromium (\( D = 0.280 \exp\left(-\frac{73,200}{RT}\right) \)) is in good accordance with that for cation diffusion in hot-pressed chromic oxide (by the same author). Also in fair agreement with the aforementioned is the work of
Sun on cation diffusivities in chromite spinel FeCr\textsubscript{2}O\textsubscript{4}. Using Cr\textsuperscript{51} tracer and a sectioning technique, he found that the diffusion of chromium in the sintered spinel was in accordance with \( D_{\text{Cr}} = 2 \exp (-70,000/RT) \).

These compatible equations for cation diffusion are in contrast to the work of Lindner and Åkerstrom\textsuperscript{72} and Ignator et al.\textsuperscript{73} on chromic oxide. Using sintered compacts of Cr\textsubscript{2}O\textsubscript{3} Lindner and Åkerstrom stated that cation diffusion followed the Arrhenius type expression \( D = 4 \times 10^3 \exp (-100,000/RT) \). Hagel found that the Arrhenius expression for cation diffusion was not substantially affected by different final oxide densities as produced by differing methods. Lindner\textsuperscript{74} concluded though, that even in the case of comparatively porous oxide samples, the high energy of activation for diffusion may be practically identical with that for bulk diffusion. Thus considering the different contributions of bulk and interface diffusion, the largest amount of diffusing material will have to negotiate well-sintered particle bridges; despite this the rate determining partial process is lattice diffusion.

Ignator et al.\textsuperscript{73} document that \( D = 4.29 \times 10^{-8} \exp (-22,000/RT) \) for cation diffusion in Cr\textsubscript{2}O\textsubscript{3} between 900°C.
and $1200^\circ\text{C}$. This relationship (low activation energy and frequency factor) is suggestive of grain boundary or surface diffusion, and/or extrinsic behaviour.

Hagel and Seybolt found higher diffusivities for $\text{Cr}^{51}$ in hot-pressed $\text{Cr}_2\text{O}_3$ which had been annealed under nitrogen to inhibit volatilisation. By using sintered samples of 93% theoretical density, the low data of Lindner and Åkerstrom could be approached.

Paladino and Coble\textsuperscript{75} have suggested that in alumina the cations may be actually rate controlling in a sintering process, because of greatly enhanced grain boundary anion diffusion.

The divergence between cation and anion diffusion coefficients in $\text{Cr}_2\text{O}_3$ enables a more direct mechanistic understanding to be obtained, than in the case of say $\text{Al}_2\text{O}_3$ where there is not a great difference between anion and cation mobilities.
General:

Sufficient chromium oxide (B.D.H., laboratory grade) of one batch was obtained for most of the experimental work, since there was evidence that interbatch variation slightly influenced densification. This powder was analysed as regards impurity content and particle size distribution, and divided into size fractions.

Densification-time curves were obtained at various temperatures for all fractions, the relationships found between densification, time, temperature and average particle size being used to indicate the processes occurring.

The effect of sintering atmosphere (composition, pressure) was studied, as was the diffusion of chromium in both the plain and 'activated' oxide by tracer techniques.

In the following pages, the techniques attempted and used for classifying the powder, determining the surface areas and particle shape, and detecting impurities are first described and followed by an account of the techniques used in sintering studies and diffusion work. A limited
Classification of Oxide Powders into Specific Fractions:

1. Aqueous Dispersion and Classification.

The first method to be examined was simple sedimentation of the oxide in water. The procedure consisted of repeated sedimentation and decantation of the dispersed oxide. The oxide powder (not greater than two percent w/weight of water) was dispersed in water in a tall beaker and allowed to settle for a time corresponding to the largest size selected. The procedure is not applicable for particle sizes less than about 5 μ. At the end of this time, the supernatant liquid was decanted into a separate beaker where again the solid was allowed to settle out. This process was repeated six times with six separate beakers. Settling times taken were 1, 2, 4, 8, and 16 minutes. It was shown by Heywood that a 90% separation of particles smaller than the selected size was given by 11 washing-decantations. In fact, 8 washings were conducted.

On examining the separated fractions microscopically, it was observed that they consisted not of discrete particles
of oxide but of an agglomeration of particles. This applied to fractions for all decantation times.

Severe flocculation of the dispersed oxide was observed during settling. In an attempt to offset this and to achieve an intrinsic separation, the Blythe method of dynamic elutriation was used and the Cummings method discontinued.

The Blythe elutriator utilises six beakers almost filled with water and connected in series by siphons; the diameter of the up-going tube of each siphon was \(\sqrt{2}\) times that of the preceding one. Each of the beakers was mechanically stirred, and water from a constant-head tank flowed at a controlled rate through the system.

The dispersed powder was washed into the first beaker, where the coarsest particles or agglomeration were retained. All particles below a specific size, determined by the water velocity of the first siphon, were carried over to the second beaker. The entraining velocity in the second siphon was only half that of the first so that, again, the coarser particles remained in the second beaker and the finer ones were carried along. It was thus theoretically possible to separate the powder into seven fractions. Given careful control it was ideally possible to fractionate
down to a particle size of not less than five microns.

However, microscopic examination of the fraction showed that there was excessive particle agglomeration, which gave rise to pseudo particles having a shorter sedimenting time than individual particles. The flocculation occurred in all the elutriating beakers of the Blythe apparatus.

To reduce the tendency of the oxide powder to flocculate during elutriation, it was decided to investigate the possibility of suitable dispersing agents and their possible deleterious effect on the sintering process. Of the inorganic reagents used, (weak acid salts of the alkali metals) sodium silicate proved to be far and above the most effective. Other dispersants tried were sodium carbonate, cyanide, sulphide and triphosphate; pH control was also investigated.

The disadvantage of sodium silicate as a dispersant is that, having been adsorbed on to the particle surface, it will react with atmospheric carbon dioxide, leaving a silica coating on the chromic oxide particles. To obviate this, a sample of oxide, having been dispersed with 0.1 wt% silicate was washed with water, then dried, admixed with carbon activator, pressed and sintered.
The sintering rate differed from that of the control oxide (washed without dispersant) indicating that desorption of silicate from the oxide surface was incomplete. Repeated washings had the effect of bringing the sintered density of the dispersed powder to an asymptotic value that was greater than that of the control oxide sintered density. It was evident therefore that the physisorption of $\text{SiO}_2^-$ on to the chromic oxide surface was not completely reversible and that not all the silicate could be removed by washing.

Of the organic dispersing agents tried, proprietary names, - Aerosol O.T. and Lissapol N., - the former only was an effective dispersant. This long chain ether - as well as other anionic dispersing agents such as alkyl benzene sulphonate - in concentrations of 0.1 wt% with water proved effective in dispersing the chromic oxide (5% suspension).

It was necessary to examine the degree to which the surfactant, having dispersed the powder could be removed. Similar experiments to those using sodium silicate as dispersant were conducted, and it was found that the surface active agent could not be removed sufficiently completely for the sintered densities of activated oxide with and without surfactant to be identical (sintering under identical times and temperatures).
Cross Section Of Mikroplex Classifier.

a, Gravity feed duct.
b, Rotating classifying chamber.
c, Variable guide vanes.
d, Cutting edge for "heavies".
e, Discharge screw.
f, Air entrance.
g, Axial opening for fines-air mixture.
The production of classified oxide fractions by means of liquid elutriation with a dispersing surfactant addition was therefore abandoned.

2. *Air Classification.*

Classification into three fractions was achieved finally by means of a spiral centrifugal air classifier. This work was conducted on a "Mikroplex" air classifier, in conjunction with the Morgan Crucible Co. Ltd. This classifier differs from the more conventional circulating-air gravity separators in its use of rotating classifying chamber walls\(^{78,79}\). Feed material is introduced through a gravity duct on to the periphery of the classifying chamber. The air enters through a duct parallel to the feed duct, entrapping the powder particles and conveying them into the classifying chamber, where separation occurs. Flow lines of the particles approximate to Archimedian spirals.

The coarse material circulating at the outside of the classifying chamber is skimmed off by a cutting edge and discharged by a worm screw. The fines, which describe a spiral path towards the centre of the classifying chamber, escape with the air carrier through a central axial opening. The radial velocity of the particles in the classifying chamber is inversely proportional to their particle radius.
The slope of the spiral path within the classifying chamber is therefore a function of the particle size.

Co-axial with the classifying chamber is a fan that produces the fine material conveyance and entire air for the separation process.

The fineness of separation is, above all, influenced by the adjustable guiding vanes. These vanes dictate the angle at which the air strikes the classifying chamber periphery. The vanes are adjustable between zero and 15°—the angle between inflow direction and classifying chamber tangent. With increasing steepness of vane setting the cut size becomes more coarse. The rotational speed of the classifier has but a slight influence on the cut fineness. Cut is also dependent to a limited extent upon character of feed material.

Although the published separation limits for this spiral air classifier are 3 μ to 50 μ, separation was conducted on a batch of chromic oxide having a specific surface (B.E.T. of 3.75 m²g⁻¹) which gives a geometric mean diameter of 0.308 μ. Despite the fact that this was well below the minimum size limit, separation was effected into three size fractions that were subsequently used in the sintering study.
Apparatus For Measurement Of Surface Area.

Fig 5
It was apparent from the surface areas of the separated fractions that the higher surface area fraction (4.3 m$^2$g$^{-1}$) was approaching the separation limit of the classifier.

Measurements of Surface Area:

The surface areas of all the samples of chromic oxide powder used in the sintering work were determined by means of the krypton adsorption method. Examination of the projected areas and size-frequency distributions were also made utilising both projection and electron microscopes.

1. Krypton Adsorption.

The adsorption of krypton at liquid nitrogen temperatures was measured, using the B.E.T. theory to interpret the results. The design of the apparatus is shown in Figs. 5 and 6. This apparatus consists essentially of a McLeod gauge, a doser volume, a reservoir for the krypton and a sorption bulb. The McLeod gauge was of a special design which allowed the pressure of the gas enclosed in the bulb to be measured against a high vacuum instead of the more normal technique of measuring the pressure against the pressure existing in the doser volume. This design results in a linear relationship between scale reading and doser pressure. This doser volume includes the McLeod gauge and the volume confined within taps.
The McLeod gauge was calibrated to the cut-off with mercury, as was the sorption bulb to the mark A.

The doser volume to $T_5$ was calibrated by cutting off a known volume of gas at a known pressure in the McLeod gauge, and expanding this dose into the whole of the evacuated system; the residual pressure was measured. From the decrease in pressure and assuming Boyle's law to be obeyed, the total volume, including the McLeod gauge, to $T_5$ was calculated. On repeating this procedure with the tap $T_5$ open, the total system volume, including the sorption bulb, was determined. Since the volume of the sorption bulb and of the oxide sample was known, the volume from $T_5$ to mark A was obtained by difference. These system volumes were found to an estimated accuracy of $\pm 0.5\%$.

Oxide samples were outgassed for at least twelve hours at ambient atmospheric temperature. Liquid nitrogen was placed around the sorption cell to mark A and the whole system allowed to equilibrate thermally for at least one hour before a krypton adsorption isotherm was measured. At the same time the side arm in the reservoir of krypton was surrounded by liquid nitrogen taken from the same batch as that used to surround the sorption bulb.
The following procedure was adopted for obtaining data for an isotherm. A sample of krypton (supplied by British Oxygen Ltd. stated to be 99.5-100% krypton, balance xenon) was introduced into the system from the reservoir with $T_2$ and $T_5$ closed. The pressure of this dose was measured. $T_5$ was opened and the system left for one hour to reach equilibrium. $T_5$ was then closed and the pressure of the gas in the doser volume measured. A second dose was introduced into the system, its pressure measured, $T_5$ opened and the system left for half an hour to reach equilibrium. The third and successive doses were left for a quarter of an hour only before equilibrium was obtained.

From the B.E.T. theory one obtains the empirical formula:

$$\frac{p}{V(p_0-p)} = \frac{1}{V_mC} + \frac{C-1}{V_mC} \left(\frac{p}{p_0}\right)$$

Where $p_0$ is the saturated vapour pressure of supercooled liquid krypton at liquid nitrogen temperature, $p$ is the true equilibrium pressure over the oxide at this temperature; $V$ is the volume of gas adsorbed in mls. converted to N.T.P.; $V_m$ is the volume of krypton required to cover a monolayer, and $C$ is a constant. Hence by plotting $\left[\frac{p}{V(p_0-p)}\right]$ against $\left[\frac{p}{p_0}\right]$, it is possible to obtain $V_m$ directly, from the relationship: $V_m = (\text{slope} + \text{intercept})^{-1}$. 


The temperature of the liquid nitrogen bath was determined from the vapour pressure of the krypton in the storage bulb. Tap $T_5$ was opened some fifteen minutes after the liquid nitrogen bath had been placed round the side arm of the krypton storage bulb. The vapour pressure of the solid krypton in the storage bulb was measured on the McLeod gauge, and from a graph of vapour pressure of solid krypton versus temperature, the temperature of the liquid nitrogen bath was interpolated.

The measured equilibrium pressure, $P_m$ mm Hg, existing over the sorbent, has to be corrected for the thermal transpiration. The true equilibrium pressure, $P$ mm Hg, over the crystals at liquid nitrogen temperature, was shown by Rosenberg to be:

$$P = P_m \left[ 1 - \frac{0.490}{37.2D^2(P_m)^2 + 14.45DP_m + 1} \right]$$

Where $D$ is the diameter of the tubing in mm over which the thermal gradient occurs. In the system used $D$ was 3 mm and the equation significant when $P_mD > 0.07$ mm Hg.

To calculate the specific surface (weight basis) from $V_m$ is relatively simple since:

$$n_m = \frac{V_m N_s}{22.414 \times 10^3}$$

Where $n_m$ is the number of molecules to cover a particulate
monolayer. \( N \) is Avogadro's Number.

If the cross-sectional area of a krypton molecule is \( \sigma_{Kr} \), and the weight of oxide sample is \( W \) gms, then the specific surface \( A, \text{ cm}^2\text{g}^{-1} \), is given by:

\[
A = \frac{V \cdot N \cdot \sigma_{Kr}}{22.414 \times 10^3 \cdot W}
\]

A value of \( 19.5 \Omega^2 \) was taken for \( \sigma_{Kr} \). This value, although higher than that calculated from the close packed liquid or solid was suggested by Beebe et al.\(^{35}\) in comparing nitrogen and krypton adsorption on the same surfaces.

2. **Visual Methods: Optical Microscopy.**

Photomicrographs were taken of projected areas of the oxide samples, on a Vickers standard projection microscope. Oxide samples were dispersed by means of a drop of surface active agent (Aerosol O.T.), on a glass slide, dried, and transmission shadowgraphs taken from them. The microscope was operated at a magnification of \( \times 1,000 \). At this magnification, projected particulate diameters of one \( \mu \) would appear on the screen with an effective diameter of \( 1 \text{ mm} \).

Since the projection microscope was operating at relatively high magnification demanding both good resolution and depth of focus, the light was rendered monochromatic
by means of a green filter interposed between the collimator and objective lens. The aperture was closed commensurate with good depth of focus. This was necessary in view of the differential between objective to particle distance with particles of widely differing sizes. To maintain statistical validity at least 700 particles were counted in each batch analysed. Size groupings were plotted on a percentage basis so as to obtain histogram size-frequency (number basis) distributions, and cumulative size-frequency (number basis) distributions. From these distributions were obtained the arithmetic mean and median particle diameters respectively. The asymmetry "A" of the size-frequency distribution is defined by:

\[ A = \frac{3 \text{mean} - \text{median}}{\sigma} \]

where \( \sigma \) is the standard deviation. From the degree of asymmetry obtained it was necessary to apply the Hatche-Choate equation relating specific surface to particle diameter and size distribution. A size distribution having a geometric mean diameter \( d_g \), log geometric standard deviation \( \sigma_g \); surface and volume shape factors \( a_s \) and \( a_v \) respectively, and density \( \rho \) is related to the specific surface \( S_w \) by:

\[ \log S_w = \log \frac{a_s}{\rho a_v} - 5.757 \log d_g - 5.757 \log^2 \sigma_g \]
simplifying this for spherical equivalents, when \( \alpha_s = \pi \)
and \( \alpha_v = \pi/6 \) then,

\[
\log S_w = \log \frac{6}{\rho} - \log d - 5.757 \log \sigma_g
\]

This relationship was used to obtain specific surface areas
on a weight basis that were complementary to those obtained
by krypton adsorption methods.

**Electron Microscopy:**

Samples of differing oxide batches and sintered
oxide specimens both activated and unactivated were examined
and classified by the transmission technique on an A.E.I.
EM6G electron microscope. Sintered samples were examined
by means of a two-stage plastic carbon replica\(^{87}\), while
for the oxide powder classification, a single stage only,
plain carbon shadow was satisfactory\(^{88}\). The particles of
all oxide batches used in the sintering experiments were
examined, at both high and, where necessary, low
magnification (as shown). The powders were dispersed by
a surface active agent and ultrasonic agitation. A smear
was drawn across a prepared glass slide, dried, shadowed
with carbon and floated off on water. The powder entrapped
within the carbon film was mounted on a copper grid
("Athene 200") and examined. It was found necessary to
use a carbon mounting for the powders, as without a suitable
electric earth, the particles attained a charge in the electron beam, thereby deflecting it and causing image instability. This was found to occur when a formvar mounting medium was used.

Sintered oxide specimens - both activated and unactivated - were sectioned, polished and etched before replication. An attempt was made to delineate microscopic heterogeneities by selective etching of the polished surface. Grease transferred during the polishing operation was removed by boiling in carbon tetrachloride. Grain structure was outlined by boiling the degreased compact in concentrated sodium hydroxide. To inhibit the formation of a gelatinous precipitate within the sintered structure, the sodium hydroxide was neutralised with hydrochloric acid. The compact was then washed in water, acetone and dried. Though this technique was in part successful it gave inferior results to thermal etching in vacuo, which was subsequently used on the majority of specimens. This consisted of subjecting the polished surface to a temperature of 1400°C for two minutes at a pressure of one μHg.

Replication of the surface so obtained was effected by Bex film steeped in acetone. This was allowed to dry in contact with the etched surface. The film was stripped
from the oxide, shadowed with carbon and finally leached with acetone. Leaching with acetone from a burette was found to expedite the removal of the Bex film better than merely steeping the film in a bath of solvent. Removal of the plastic film was, additionally, more complete.

In the instances where sintering had occurred to a minimal extent - in the lower temperature pure oxide sinters - it was possible to obtain extraction replicas of the sintered surfaces. The oxide particles were physically detached by the Bex film. This "replica" was shadowed, leached and examined as before. In the image obtained - being that of a projected area - it was possible - with selective application - to discern the silhouette of the "necked" particle interface, this being representative of the degree of sintering.

Spectroscopic Analysis:

For the analysis of the impurity levels found in "Lab Grade" chromic oxide it was necessary to resort to emission spectroscopy, chemical methods of analysis being of insufficient sensitivity for the low impurity content subsequently found to exist. The analysis was made using a Hilger quartz prism spectrograph. The required exposure was found to be of the order of 60 seconds for the D.C. arc
used. Both visible and ultra violet emission lines were examined and compared against standards of spectroscopically pure elements. The suspected elements likely to be responsible for variation in the sintering rates of the activated oxide were iron, sulphur, silicon and molybdenum, and these elements were run as control standards in the analysis. It was necessary to have a standard for carbon in the spectrum for comparison and elimination. The spectral lines of carbon would of necessity appear in the arcing of chromic oxide between two carbon electrodes - together with the lines of chromium. Since the work was qualitative, plates were not standardised with regard to line density as a function of total exposure. Spectra of carbon, chromic oxide and the control of the suspected impurity were exposed on the same plate in close proximity to one another. This was effected by utilising the Hartmann diaphragm on the spectrograph; spectral lines of constant wavelength for the different elements were then found in the same relative position on the photographic plate.

As the impurity levels were low only the most intense lines were observable, and it was these "ultimate lines" (R.U.) that were used in positively identifying the impurity elements in the oxide.
Initially, in detecting the impurities, an iron spectrum was exposed in proximity with the oxide spectrum. The wavelengths of the trace ultimate lines were determined by linear interpolation from specific known iron spectral lines. Iron was selected as a reference because of its particularly rich spectrum. Accurate interpolation of the line position was obtained with a comparator. This procedure was applied only over a narrow band of wavelength of not more than twenty angstroms, as the linear reciprocal dispersion is essentially dependant on wavelength for a prism spectrometer. All the standards used were spectroscopically pure; the metal standards were used in rod form for both electrodes, there was therefore no interfering continuous emission band from carbon.

Since it was necessary to arc the oxide between two graphite electrodes, careful adjustment of the operating characteristics of the arc was required to obviate interference from the cyanogen bands: this emission being particularly strong in the region 3500 to 4200 angstroms.

Confirmatory work was carried out on three different oxide batches by means of the mass spectrometer. As it was necessary to use an instrument amenable to material of low vapour pressure, the r.f. spark mass spectrometer, A.E.I type M.S.7 was used.
This instrument enabled not only a more comprehensive qualitative assessment of trace impurities, but also a quantitative determination superior to that obtainable by spectroscopic methods.

In both spectroscopic and mass spectrometric methods, sensitivities for the evaluation of trace levels varies from one element to another, and the quantitative determination must therefore be considered with this reservation in mind. Minimum impurity concentrations down to ten parts per million were noted by this latter method.

The mass spectrometric analysis was kindly carried out by the Admiralty Materials Laboratory, Holton Heath.

X-ray Diffraction Analysis:

In the analysis of oxide powders by the Debye-Scherrer technique, three oxide samples were used. The first two powders were oxides of different batches, while the third was one of the batches, having first been pre-annealed at 850°C for half an hour in vacuo. The oxides were mounted on glass fibre rods with fish glue. Using a 9 cm Unicam camera and nickel filtered Cu-Kα radiation, Debye rings were obtained after exposures of the order of three hours. All films were
exposed and developed for identical times in an attempt to maintain constancy in the comparison of line densities. Owing to the strong fluorescence of chromium, by excitation from the X-ray beam, considerable fogging of the film by "white radiation" was observed.

**Experimental Materials:**

All oxide was dried in a desiccator for at least 24 hours. The analyses - particulate and chemical - of all the oxides used in the sintering work are given in Fig. 11 and 27 respectively.

**Activating Agents:**

The activating-reducing agent admixed with the chromic oxide in all the work herein undertaken was carbon. Of the various forms available, "Shell" carbon proved to be the most suitable. It is characterised by a high specific surface area and high purity. This carbon, obtained by courtesy of Murex Ltd., was examined for its approximate size distribution and mean particulate size by electron microscopy.

The effect of other different carbon types - namely graphite, charcoal and colloidal graphite (the latter ex-Graphite Products Ltd., S.W.18) on the sintering rate and
final sintered density was examined. No experimental difficulties were experienced with the graphites, but they would be expected to be less fine than the "Shell" carbon. Activated charcoal was unsuitable in so far as it made pressing of the green compacts difficult, (Stone Ph.D. thesis)\textsuperscript{66}. The use of this was consequently abandoned.

Mixing and Pressing:

All determinations for the isothermal sintering work were carried out in duplicate as a minimum requirement.

All work was executed using a constant amount ($\frac{1}{2}$ wt\%) of carbon, admixed with the chromic oxide. The powders for pressing were made up in lots of 100 gms. to increase reproducibility and expedite the work.

The carbon was introduced to the chromic oxide by mixing intimately, care being taken to produce an homogenous mix and thoroughly disintegrate the oxide agglomerate\textsuperscript{66}.

Individual compacts of chromic oxide and carbon were made by weighing out $\frac{1}{2}$ gm. of powder mixture and pressing dry and cold in a double acting die of $\frac{3}{8}$" diameter. The pressing pressure was maintained constant at 8 tons/sq" - the hydraulic press being calibrated at regular intervals. (See Stone and Lockington "Powder Metallurgy")\textsuperscript{65}. Pressing
and ejecting of the compacts was such that no difficulty was experienced in all the powders used, an exception being the ultrapure chromic oxide used in one series of experiments. This was considered to be due to the high surface area of the powder, enabling it to penetrate the interstice between the die mandrel and block.

Linear dimensional changes of the compact were observed by measuring the axial and diametric changes of the compact, before and after sintering, with a micrometer screw gauge. Linear shrinkage was found to be isotropic so that one reading of length and diameter change sufficed. Weights before and after sintering were also recorded, although not of primary relevance to the work herein undertaken.

Sintering:

In the determination of isothermal sintering data, a horizontal platinum resistance furnace was used. This furnace was capable of operation intermittently up to 1600°C and continuously up to 1550°C. At these temperatures it was necessary to use recrystallised alumina for the refractory furnace tube, the ends of which were ground so as to accommodate "0" ring type seals and vacuum flanges - as shown in the photograph, Fig.8. The furnace tube was evacuated by means of a combination of oil diffusion and
rotary backing pumps, which enabled an absolute vacuum of $10^{-4}$ mm to be obtained. Vacuum was measured by a Philips cold cathode gauge, and a McLeod gauge connected to one of the furnace tube vacuum flanges; provision was made for controlling the vacuum by a double needle valve (two needle valves in series providing more precise control).

The furnace and controller as supplied by Johnson, Matthey and Co. Ltd. was equipped with only an energy controller— the temperature recorded being that of the furnace resistance windings, which were in direct contact with the thermocouple. To ensure precise and constant temperature control it proved necessary to add a "Transitrol" controller, in conjunction with an alumina sheathed control thermocouple placed axially down the furnace tube. It was necessary to calibrate the hot zone of the furnace, and this was done for all the temperatures that were used in the isothermal sintering, i.e. 1000°C to 1550°C. The zone was of constant temperature, $\pm 2^\circ$C, for not less than five centimetres at all temperatures. It was in this calibrated zone that the thermocouple (Pt, Pt - 13% Rh) was placed, and in which sintering was effected. Temperature control was estimated to be accurate to $\pm 5^\circ$C. At regular intervals the thermocouple was checked against a standard in case of contamination. The coin shaped compacts were
supported upon and within a tungsten coil which was attached to a tungsten rod that was operable externally. The rod passed axially through the end vacuum flange - vacuum tightness being obtained by a double "O" ring type seal. The vacuum flange was demountable to facilitate introduction of specimens.

Initially, molybdenum wire was used for the specimen supporting coil but it was shown by spectroscopic analysis that trace pick up occurred during a sintering run, so that to obviate any possibility of contamination it was replaced by tungsten with a correspondingly lower vapour pressure at the same temperature.

A compact weight of half a gram was chosen for two main reasons. Firstly, to obviate error in heating up in the hot zone (thermal inertia), and to reduce the thermal shock imposed on the alumina refractory tube. By reducing the compact size as much as possible to a coin shape the thermal inertia and consequently the heating up period were minimised. The error involved in heating the compact from 20°C to the operating ambient temperature was found by observation to be twenty seconds. The compact on introduction into the hot zone was observed through a glass window set in the end of the vacuum flange - the time taken for there
to be no discernable colour difference between the furnace tube and compact was taken to be the heating up time. This time was deducted from the time of isothermal sintering of the compact. A third reason for choosing a low compact weight was that gas evolution from a specimen size greater than one gram resulted in saturation of the diffusion pump backing line, thus rendering the pump temporarily ineffective.

With a specimen weight of $\frac{1}{2}$ gram the vacuum level returned to its initial state within two minutes. Experiments conducted on the variation of sintering rate with oxygen partial pressure showed that within a fifty-fold increase above the static vacuum level the sintering rate was unaffected.

The hot zone temperature was observed to drop by about ten degrees when the cold compact was introduced at the beginning of a sintering run. This was corrected by the controller, when the temperature would return to the required value within about twenty seconds.

A typical sintering run would consist of drying the compact in a dessicator for 24 hours, introducing it into the furnace mounted on the tungsten coil. The vacuum, first roughed by the rotary pump, was finally brought to $5 \times 10^{-4}$ mm with the diffusion pump. The specimen was introduced into the hot zone by means of the pusher rod, sintered for the
required time and withdrawn to the cold zone by the same means; cooling to below 1000°C (when sintering is negligible) occurred in an estimated time of not more than five seconds.

Sintering was also done with an inert gas (argon) instead of a vacuum. The gas for these runs was first dried with silica gel and finally by phosphorus pentoxide in a porous medium.

Gravimetric Analysis for Residual Carbon in Sintered Compacts:

Analysis of carbon activated sintered compacts for residual carbon was carried out using a combustion type apparatus. The specimens of sintered oxide chosen for analysis had been sintered at 1400°C for graphically representative times from 2 to 50 minutes, this embraces a period in which the sintering rate decreases effectively to zero.

Oxygen at a pressure of one pound per square inch and flow rate of 300 ml. per minute was dried by soda asbestos and magnesium perchlorate towers. This dry oxygen was passed through a tube furnace at 1000°C within which was contained the crushed (-250 mesh) presintered compact. The resultant gases, consisting of excess oxygen, carbon dioxide and sulphur dioxide, passed through sorption towers and a preweighed sorption bulb. A final drying tower was situated between the
issuing residual gases and the atmosphere. This prevented any absorption of atmospheric water vapour during the reaction period. To ensure complete combustion of the carbon the oxygen flow was maintained for a period of ten minutes. Control runs were made thus obviating possible error due to combustible material in the oxide and porcelain boat giving a spurious result. The control consisted of an equivalent quantity of pre-dried chromic oxide without any carbon addition.

In addition to this analytical technique, the results obtained were confirmed by a modified gravimetric apparatus similar in design but differing in detail. Instead of the combustion products being absorbed by soda asbestos and magnesium perchlorate they were selectively removed by freezing out. This analysis was conducted by the research department of Richard, Thomas and Baldwin Ltd.

Determination of Diffusion Coefficients:

Counting Equipment and Techniques.

All the isotopes used were counted in an Ekco, solid, well type scintillation counter. The scintillation phosphor was of tantalum doped sodium iodide. Pulses from this scintillator were preamplified (Ekco N640A) and fed into an
Ekco Scaler and Discriminator (type N530 C).

Chromium 51, with the comparatively long half life of 27 days allowed counting to be made on a constant count rather than on a constant time basis.

The total dead time of the counting circuit was two microsecs. The number of counts recorded on the scaler were corrected, where necessary, for this dead time by the usual equation:

\[
N_t = \frac{N}{1 - N_t \cdot T}
\]

where \(N_t\) is the true number of counts per second, \(N\) the observed number of counts/sec., and \(T\) the dead time of the circuit in seconds. All counts were expressed as counts per second and corrected for random background.

Sintered composite compacts were prepared in a manner similar to that used for the isothermally sintered specimens. Irradiated chromic oxide (\(^{51}\text{Cr}_2\text{O}_3\)) of specific activity \(\frac{1}{3}\) millicurie per gram (admixed with carbon before irradiation) was cold pressed in a double acting die to 8 tons per square inch. On removal of one of the plungers from the die, an equal weight of unirradiated chromic oxide (\(\text{Cr}_2\text{O}_3\)) of the same classification and carbon addition was placed on top of the pressed powder in the die, after the method of Lindner\(^90\).
Grinding Apparatus Used In The Study Of Cation Diffusion In Chromic Oxide.
The whole was finally pressed to 8 tons per square inch, removed from the die and sintered in vacuo at the required temperature and time.

So that the results would be complementary to the isothermal shrinkages of activated oxide compacts, sintering temperatures were chosen that corresponded with the work on the respective oxide fractions.

The sintered composite was impregnated with cold setting epoxy resin and attached by this to the end of an aluminium mandrel - as shown in the diagram, Fig.7. The diameter of this mandrel was less than the diameter of the specimen. This allowed the circumference of the compact to be ground away, thus obviating any surface effect and consequently a spuriously high interdiffusion of the chromium ions.

It was possible, by means of the grinding apparatus shown, Fig.9, to grind off small sections of the order of one thousandth of an inch from the sintered composite. This was effected by the vertically mounted micrometer gauge bearing on the opposite end of the mandrel.

Considerable care was taken in the design of the grinder that location of the mandrel axis was precisely perpendicular to the face of the grinder in contact with the emery abrasive.
That this was so was shown by the lack of detectable error in the measurement of composite thickness after grinding taken at three points on the circumference.

The grinding medium was "wet and dry" emery paper, grade 360A. Too fine a grade resulted in the clogging of the surface, while the quantity of paper that could be used per grind was limited by the size of the counting container that was placed in the well scintillator.

The grinder was supported at one end by two ball bearing races, these straddled the strip of grinding paper. It was therefore necessary to provide for the thickness of the emery paper (0.008"). This was implemented by means of feeler gauges and a surface plate; correct height and parallelism then being obtained. The actual grinding was conducted on a sheet of plate glass on to which was clamped the emery grinding strip. The whole procedure was operated within a glove box.

After each grind the length and weight of the mandrel and composite were noted. The emery strip and oxide, together with any residue, which was brushed off from the grinder, were placed in the counting container. Having ground the whole compact, the activity of the individual sections were
measured on the scintillation counter already described. In view of the half life of 27 days, no half lifetime decay correction was necessary during the measurement of the activities. A background count rate was measured with an empty sample tube in situ. All samples were counted for at least 3,000 counts, so that the error in counting, $\pm N_T^{1/2}$ was not greater than $\pm 2\%$.

Since the decay of Cr$^{51}$ occurs with the emission of gamma radiation of energy 0.32 MeV, no self absorption correction was considered necessary. The geometry of the well counter with regard to the sample tube was maintained constant throughout the experiments.

Cation self-diffusion coefficients were determined from these results at five temperatures over a range from 1300°C to 1500°C. These coefficients were determined for both fine and coarse activated oxide fractions, while the unactivated pure oxide had a value deduced for only one temperature, 1450°C. Arrhenius type plots of the diffusion coefficient $D$ as a function of temperature were made (plotting $\log_{10}D$ against $\frac{1}{T}$ oK$^{-1}$). From the linear slope $-\frac{E}{2.303R}$, was determined the activation energy $E$ for cation self-diffusion.
Linear shrinkage (fractional) versus wt% carbon admixture to batch 5 chromic oxide:
Sintered at 1430°C, in vacuo, 10 minutes.

Fig 10
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<thead>
<tr>
<th>B.D.H. batch. (Lab Grade)</th>
<th>Particle fractions</th>
<th>Designation</th>
<th>Specific area (gas sorption)</th>
<th>Mean diameter (sorption)</th>
<th>Mean diameter (optical)</th>
</tr>
</thead>
<tbody>
<tr>
<td>64I2C4</td>
<td>I</td>
<td></td>
<td>3.62 m²g⁻¹</td>
<td>.302 micron</td>
<td></td>
</tr>
<tr>
<td>64I2II</td>
<td>A</td>
<td>A</td>
<td>4.16</td>
<td>.277</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>B</td>
<td>4.27</td>
<td>.270</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>C</td>
<td>2.67</td>
<td>.432</td>
<td>1.62 micron</td>
</tr>
<tr>
<td>64I2II</td>
<td>2</td>
<td></td>
<td>3.75</td>
<td>.308</td>
<td></td>
</tr>
<tr>
<td>2204II2</td>
<td>5</td>
<td></td>
<td>3.79</td>
<td>.304</td>
<td></td>
</tr>
<tr>
<td>2446740</td>
<td>3</td>
<td></td>
<td>7.42</td>
<td>.155</td>
<td></td>
</tr>
<tr>
<td>I397I (ultrapure)</td>
<td>4</td>
<td></td>
<td>9.32</td>
<td>.124</td>
<td></td>
</tr>
</tbody>
</table>

Classification of chromic oxides used in experimentation.
Effect of Carbon Content Addition upon the Sintering of Chromic Oxide:

The effect of percentage carbon addition to chromic oxide was investigated by Stone, the results of which are shown in Fig.10. It is observed that the linear shrinkage remains constant over an approximately hundred fold increase in carbon concentration in the oxide; (the minimum carbon admixture for which shrinkage occurs being about 0.1 wt%, as found in the present study). Shrinkage for carbon additions below this level tends to that of pure oxide. Although no repeat study was performed by the author, it appears that the oxide used by Stone differed little from the main oxide used in the present study. The analysis of the oxide batch used by Stone (batch 5) is given in Fig.27 for impurity level and in Fig.11 for surface area. It can be seen that the surface area differs little from that of batch 2 chromic oxide from which the main particle size separations (A, B and C) were obtained. It is permissible to compare the mode of sintering of chromic oxide studied by Stone to that of the present work. He heated the
Linear shrinkage versus time $t^{1/3}$
Sinter 1400 °C
Oxide batch 2, +1/2% carbon.

Residual carbon versus time $t^{1/3}$
Sinter 1400 °C
Oxide batch 2, +1/2% carbon.

- ○ — Combustion analysis.
- □ — Richard, Thomas & Baldwin analysis.

Fig 12
activated compact in situ in a vacuum furnace to the sintering temperature (1430°C) where he maintained it for a period of ten minutes. This treatment was subsequently found (under the present study) to effect sintering to a constant densification - as shown in the isothermal studies in Fig.14 for batch 2 chromic oxide + \( \frac{1}{2} \% \) carbon.

As a complementary study to shrinkage as a function of carbon content at constant time and temperature, the effect of residual carbon in the sintered compacts was studied as a function of time. For the sake of ease of comparison with linear shrinkage as a function of time (same scale) - the two curves are juxtaposed in Fig.12 - the x axis was plotted as the cube root of time. As can be seen from the isothermal sintering curves (Fig.13 to 18) all the different oxide batches conformed approximately, during the initial rapid sintering period, to a time law where the linear shrinkage varied as the cube root of time. Thus by plotting the y axis on a linear, and the x axis on a cube root of time, basis the linear shrinkage and carbon content at zero sintering time can be included in the plot. The combustion analysis for residual carbon in the chromic oxide, together with the analysis by Richard, Thomas and Baldwin are shown in the lower graph of Fig.12. It is seen that both the analyses are in agreement, and that the carbon content
Log, linear shrinkage versus log, time.

Isothermal sintering curves for batch I chromic oxide + 1% carbon.

Fig 13
Log<sub>10</sub> linear shrinkage versus log<sub>10</sub> time.

Isothermal sintering curves for "A" fraction chromic oxide +0.2% carbon.

Fig 15
Log, linear shrinkage versus log, time.

Isothermal sintering curves for C fraction chromic oxide + 1% carbon.
Log$_2$ linear shrinkage versus log$_{10}$ time.

Isothermal sintering curves for batch 3 chromic oxide + 1% carbon.
Log$_{10}$ linear shrinkage versus log$_{10}$ time.

Isothermal sintering curves for batch 4 chromic oxide + $\frac{1}{2}$% carbon.
falls off from an initial \( \frac{1}{2} \) to a minimum of about 0.03\% after a sinter of eight minutes at 1400\(^\circ\)C. By comparison with the curve of linear shrinkage as a function of time, it is seen that the cessation of shrinkage corresponds approximately to that point at which the carbon content in the compact approaches its minimum value. Both the shrinkage and the carbon content then remain substantially constant to the maximum time at which an assay was made (fifty minutes).

Throughout all the sintering and tracer diffusion experiments the carbon admixture to the green compacts was maintained at \( \frac{1}{2} \)wt\%, with the exception of the control experiments on pure oxide.

**Effect of Sintering Time on Isothermal Shrinkage of Chromic Oxide:**

All isothermal sinterings of oxide batches 1 to 4, together with the fractions A and C (\( \frac{1}{2} \)wt\% carbon) are shown in Figures 13 to 18.

All the isothermal curves were plotted on a \( \log_{10} \) linear shrinkage versus \( \log_{10} \) time basis.

It is observed that after an initial high rate of shrinkage the rate decreases until a point is reached, beyond which the shrinkage remains constant as a function of time.
Oxide batch 2, (control),
sintered, 1400 °C.
The higher the temperature of sintering the more rapid is the approach towards constant densification. At 1500°C in the case of the coarser particle sizes, and at temperatures as low as 1250°C in the case of the finer particle size oxides, the sintering was so rapid that a time of two minutes would suffice to induce maximum shrinkage. As the temperature of isothermal sintering was decreased the time taken to achieve a constant shrinkage increased, this trend being common to all oxides sintered with $\frac{1}{2}$% carbon admixture.

It will be observed that the maximum densification plateau achieved at any one temperature of isothermal sintering increases with temperature until a maximum value is reached. At higher sintering temperatures no further densification may be achieved. This density in the case of the larger particle size oxide corresponds to about 90% of the theoretical density (5.2 gm/cc) of pure chromic oxide.

The mode of activated sintering of chromic oxide with $\frac{1}{2}$% carbon admixture may be directly compared with that of the control oxide Fig.19, which was sintered under identical conditions without the added carbon. It is seen that this oxide sinters at a rate many orders of magnitude lower than the activated oxide at a comparable temperature; the time exponent for the linear shrinkage - time relationship, was 0.153 for the duration of sintering, (up to 1,000 minutes.)
Effect of Temperature on the Sintering of Chromic Oxide:

No control sinterings were conducted on pure chromic oxide (unactivated) as this has been covered by other authors (Hagel67 et al.). The single temperature control sintering of pure chromic oxide, (Batch 2), Fig.19, is mentioned in the previous section. It was found that above a particular temperature (never greater than 1500°C) and depending upon the oxide particle size, the initial linear period of activated densification was not recordable - the process being too rapid. To have plotted isothermal shrinkages of the activated oxides for sintering times less than two minutes with the existing techniques would have been unmeaningful. At a lower temperature than about 1300°C in the case of the coarser particle sized oxides and 1050°C in finest sized oxide, the shrinkages were sporadic; the activation reaction tending to be uncertain. It was possible in the majority of cases to obtain at least four isothermal sintering curves separated at fifty degree intervals. This enabled Arrhenius type activation plots to be made. The Fig.20 shows a plot of reciprocal absolute temperature versus log time to constant shrinkage for the oxides 1 to 4 and fractions A and C. The chromic oxide fraction B had a surface area that was so close to that of the A fraction that it was
considered unnecessary to repeat the sinterings on this oxide, as the results would have been within the experimental error of the A fraction isothermal sinterings.

It can be seen that although the points in Fig. 20, are subject to a certain degree of error, the gradients are commensurate with activation energies within the range 133-153 kcal/mole. Deviation occurred most noticeably for each oxide, at the highest temperature of sintering. That is, for the C fraction chromic oxide, the overall activation energy for the process between 1500°C and 1450°C was lower than the energy shown. Similarly for the A fraction where deviation to a lower activation energy occurs between 1450°C and 1400°C. One would expect if anything to observe a decrease of apparent activation energy towards the lower sintering temperatures, and it must therefore be supposed that these are spurious values, a consequence of the oxide's approach to complete densification. This is evidenced by the occurrence of the deviation at lower temperatures in the case of the oxide of higher surface area (A fraction).

Effect of Particle Size on the Sintering of Chromic Oxide:

Surface Areas, Optical and Krypton Methods:

The oxide fraction C was selected initially as that most amenable to optical sizing in view of its having the
Cumulative Size-Frequency Curve
For Chromic Oxide, C-Fraction.

Fig 21
Histogram, Size-Frequency Distribution
For Chromic Oxide, C-Fraction.

Fig 22
lowest surface area of all the oxides studied - as indicated by krypton adsorption estimation. The histogram of size-frequency (number basis) is represented in Fig. 22, while the cumulative size-frequency curve is shown in Fig. 21.

The arithmetic mean size was deduced to be 1.82 micron, and the median 1.75 micron from the cumulative curve. The degree of asymmetry of the size distribution is defined as $3 \left( \frac{\text{mean}}{\text{median}} \right)$, where $\sigma$ is the standard deviation. The standard deviation was found to be 0.79 from which it follows that the degree of asymmetry of the particle distribution is 0.266. From this it is taken that there is a moderate degree of askewness; the particle size may then be estimated in terms of log geometric mean particle size and log geometric standard deviation (1.70). The geometric mean particle diameter $d_g$ was found to be 1.62 micron; utilising the Hatche - Choate relationship:

$$\log S_w = \log \frac{6}{\rho} - \log d_g - 5.757 \log \sigma_g$$

and taking the density $\rho$ of chromic oxide = 5.2 g/cc, one obtains the specific surface (weight basis) $S_w = 0.352 \text{ m}^2\text{g}^{-1}$. This involves the assumption that the particles are spherical. As may be seen from the electron micrographs Fig. 40 to 43, this is not too unreasonable an approximation. In view of the disparity between the surface areas obtained by the
Typical Krypton Sorption Isotherms For Different Oxide Samples.

Fig 23
krypton sorption technique and the visual counting method, the latter was not used in any subsequent calculations. It is significant that the skewness of the distribution curve tends towards the finer particle sizes. Since the microscopical resolution is at its limit for the sizes below about half a micron it is to be expected that the technique is wanting in this region. On the other hand the gas sorption method can be expected to give a greater surface area and hence smaller mean particle size, than the intrinsic size. In despite of the apparent smoothness of the particles as shown by the electron micrographs Fig. 40 to 43, there will be inherent surface heterogeneities which will result in an apparently greater surface area by sorption methods. Three typical adsorption isotherms are shown in Fig.23, for oxides B, C and batch 4. The complete surface area analyses for all the oxides used in the present work are shown in Fig.11. It will be seen that only one analysis was made using optical methods (i.e. C fraction). Since this oxide was that with the largest mean particle size, examination of other oxides of higher surface area would only have resulted in spurious size-frequency curves, the optical microscope under optimum condition being at its limit of resolution at half a micron.
Log$_{10}$ linear shrinkage for constant time versus log$_{10}$ geometric mean particle diameter, (particle fractions A & C; batches I to 4).

Fig 24
The electron micrographs of Fig. 40 and 41 show of necessity only a very limited area of the distributed oxide at the magnification of x20,000. Nevertheless it can be clearly seen that there is a strong tendency for the particles to clump together and so hinder the resolution of individual particles. However on the whole the particles appear spherical without excessive protuberances that would have a pronounced effect in the initial stages of sintering.

The effect of particle size as a function of batch number and temperature on shrinkage is recorded in Fig. 24. To eliminate the effect of time, the log of linear shrinkage at constant time was plotted against log of mean particle diameter - as obtained from the krypton adsorption isotherms. As this comparison is meaningful only within the linear initial portion of the isothermal sintering curve a value of 0.6021 was chosen for log time so that values of linear shrinkage could be interpolated for all the sintering times and batches. A theoretical gradient of $\frac{4}{3}$ has been drawn on the graph for ease of comparison with the isothermal lines between differing oxide batches. It is seen that points at constant temperature for different batches can in the majority be joined by a single isotherm whose gradient increases as the temperature of the isothermal decreases. The gradient at 1400°C is $\frac{4}{3}$, and at lower temperatures it
is greater; while it is observed that at 1450°C the gradient is 1.09.

The batch of chromic oxide "2" from which the fractions A and C were separated can be seen (Fig. 24) to sinter for any constant temperature at a rate intermediate between that of its component fractions A and C. The oxide batch 3, though of greater surface area nevertheless sinters at a rate compatible with the two isotherms at 1350°C and 1300°C. However, batch 1 - virtually identical in particle size to batch 2, exhibits a distinctly and consistently lower rate of shrinkage than that which is to be expected from the isotherms.

The batch 4 - ultrapure oxide - was unfortunately of such high surface area and consequently sintering rate, that it was only possible to draw in one isotherm at 1200°C conjoining with oxide batch 3. This gradient was greater than the theoretical $\frac{4}{3}$ but not far removed from that of the isotherm between batch 1 and oxide fraction A.

The overall effect of a decrease in particle size is therefore to increase the rate of linear shrinkage at constant temperature, for all the oxides studied with the significant exception of oxide batch 1.
Log of linear shrinkage versus total systemal pressure.
Oxide batch 2 (+1/2% carbon), sintered 1400 °C, 10 minutes.

Fig 25
Effect of Atmosphere and Varying Oxygen Partial Pressure on the Sintering of Chromic Oxide:

Fig. 25 shows the effect of controlled systemic pressure on the shrinkage rate of batch 2 chromic oxide + $\frac{1}{2}$% carbon. The temperature selected was 1400°C and the sintering time, ten minutes. This enables the compact to sinter to the densification plateau as shown by the isothermal curve Fig. 14. The shrinkage is seen to remain constant over a tenfold increase in systemic pressure, and thereafter fall steadily to about 6% at 1 mm vacuum. Complementary to the variation of oxygen partial pressure on the sintering rate was a study of the effect of an argon atmosphere upon the sintering of chromic oxide. The sintering was effected under a dry argon stream at one atmosphere pressure - the oxygen and nitrogen contents being not more than 2 and 5 parts per million respectively. The results were sporadic and in no way approached those obtained by sintering in vacuum either in degree or consistency. The linear shrinkages of batch 2 chromic oxide + $\frac{1}{2}$% carbon at 1400°C in dry argon are given in the table below,
Oxide batch 2, sintered in dry hydrogen,

in atmosphere at 1400 °C.
Table of effect of argon atmosphere on sintering rate of activated chromic oxide.

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>Linear shrinkage</th>
<th>log(_{10}) linear shrinkage</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>.0373</td>
<td>3.5717</td>
</tr>
<tr>
<td>2</td>
<td>.0341</td>
<td>3.5328</td>
</tr>
<tr>
<td>10</td>
<td>.00958</td>
<td>3.9814</td>
</tr>
<tr>
<td>10</td>
<td>.0373</td>
<td>3.5717</td>
</tr>
<tr>
<td>30</td>
<td>.0373</td>
<td>3.5717</td>
</tr>
<tr>
<td>32</td>
<td>.0266</td>
<td>3.4249</td>
</tr>
<tr>
<td>60</td>
<td>.0341</td>
<td>3.5328</td>
</tr>
<tr>
<td>60</td>
<td>.0266</td>
<td>3.4249</td>
</tr>
<tr>
<td>120</td>
<td>.0266</td>
<td>3.4249</td>
</tr>
<tr>
<td>180</td>
<td>.0319</td>
<td>3.5038</td>
</tr>
</tbody>
</table>

For a comparison with the use of carbon, hydrogen was used as an activating agent in the sintering of chromic oxide.

**Hydrogen Atmosphere:**

Dry hydrogen was passed at one atmosphere pressure at 1400°C over batch 2 chromic oxide pressed in the standard manner but, without any carbon addition. The isothermal sintering curve is shown in Fig. 26. Comparing this curve with that of Fig. 14 of batch 2 chromic oxide + \(\frac{1}{2}\)% carbon.
<table>
<thead>
<tr>
<th>Impurity levels</th>
<th>Oxide 5</th>
<th>Oxide 3</th>
<th>Oxide I</th>
<th>Oxide 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.5.m. weight</td>
<td></td>
<td></td>
<td></td>
<td>Na 5 p.p.m. Si 2 p.p.m.</td>
</tr>
<tr>
<td>0-10</td>
<td>As, Zn, Cu, Ni Mn, Ti, P, Al</td>
<td>As, Zn, Ni, V, P</td>
<td>As, Zn, Cu, Ni Mn, Ti, P, B</td>
<td></td>
</tr>
<tr>
<td>10-100</td>
<td>V, K Fe 210 p.p.m.</td>
<td>Ti, K Fe 280 p.p.m.</td>
<td>K, Al Fe 280 p.p.m.</td>
<td></td>
</tr>
<tr>
<td>100-500</td>
<td>Ca, Mg, Na</td>
<td>Al</td>
<td></td>
<td></td>
</tr>
<tr>
<td>500-1000</td>
<td>S, Si 1400 p.p.m.</td>
<td>Ca, S, Mg, Na</td>
<td>V, Ca, S, Mg, Na</td>
<td>Si 2200 p.p.m.</td>
</tr>
<tr>
<td>1000-2500</td>
<td></td>
<td>Ca, S, Mg, Na</td>
<td>Si 2000 p.p.m.</td>
<td>Si 2200 p.p.m.</td>
</tr>
</tbody>
</table>

**Chemical analysis of chromic oxides used in experimentation.**

*(mass spectrometer)*

**Fig 27**
sintered at 1400°C, it is immediately apparent that although the sintering rate is slightly reduced in the case of hydrogen, no densification plateau is reached (within the maximum time of 300 minutes). The time exponent approximates to the $\frac{1}{3}$ obtained in the case of carbon activation. This illustrates therefore, that so long as there is a continuous renewal of activating agent, densification will proceed continuously.

**Effect of Impurity upon Sintering of Chromic Oxide:**

The analyses of trace impurities of four of the oxide batches used in the sintering experiments are given in Fig. 27. These analyses were performed on an r.f. mass spectrometer. The spectroscopic analysis, which was tentative and qualitative, was carried out on batches 3 and 5. These were batches which at the outset of the present work, presented different sintering rates which warranted a cursory investigation of impurity levels. Iron, sulphur and silicon were identified in both these oxides on a qualitative basis; this work was confirmed by the quantitative and more comprehensive analysis obtained by the r.f. mass spectrometer. The analyses are not absolute, as the elements possess varying sensitivities, but they provide relative estimation of the impurities within a factor.
of times three. The oxide batch 4 was an ultrapure material of high surface area and had the low impurity level shown in Fig. 27. This analysis was that given by the manufacturer and was stated to have been also conducted by mass spectrometer.

It is significant that the three oxides, batches 5, 3 and 1, all contain Ca, Mg, Na, S and Si in the range 500 to 2500 p.p.m., whereas the only oxide containing vanadium in the same range is batch 1. It is this oxide that exhibits the anomalous sintering rate shown in Fig. 24, (log shrinkage versus log particle diameter).

Iron and silicon were originally thought to have had some relevance to the differing sintering rates of the oxides, and so these two elements were analysed more accurately as shown in Fig. 27.

X-ray Analysis of Chromic Oxides:

Three oxides - batch 1, 3 and batch 3 preannealed (½ hour, 850°C, in vacuo) - were analysed for lattice strain that could have accounted for different batch activity during sintering. Two possible effects, due to particle strain or particle size, could account for Debye ring broadening, (Hall and Williamson). The particle size
Effect, significant below about 1000 angstroms, is constant throughout the diffraction rings for all angles $\theta$. The effect of lattice strain however, becomes apparent only at high $\theta$ values. Thus by comparing the diffuseness of the Debye rings at high and low $\theta$ one can obtain an indication of the state of lattice strain. Examination of the diffraction rings of the three chromic oxide samples revealed no difference - on a qualitative basis - between either the line densities at high and low $\theta$ angles or between the oxide samples selected. This suggests 1) that the annealed oxide differed little from the unannealed oxide batch 3, (from lattice strain); 2) that the batch 1 was similar to batch 3 (from strain aspect); and 3) that the mean particle sizes of the oxides were sufficiently greater than 1000 angstroms to give no discernable line broadening. This was further evidenced by the krypton surface area measurements, when the batches 1 and 3 were found to have mean particle sizes of 0.30 and 0.16 micron. 1000 angstroms is considered to be the limit of particle size below which line broadening begins to be detectable.$^{93}$

Measurement of Cation Diffusion Rates in Chromic Oxide with and without $\frac{1}{2}$% carbon admixture:

Fick's second law of diffusion may be stated in the
form \[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2},
\]
where \(D\) the diffusion coefficient is independent of concentration \(c\). This equation, involving partial derivatives, has a definite solution only if the following conditions can be fulfilled, 1) the initial conditions fixing the state of the system before diffusion \((t = 0)\); 2) the boundary conditions such as the geometric factors defining the experimental conditions (specimen thickness).

In the present work diffusion occurs between two oxide compacts mutually in contact, the one irradiated to a predetermined level \((c = c_0)\) and the other unirradiated \((c = 0)\). Under these conditions the species are diffusing, for the time, temperature and diffusion coefficients concerned, in a specimen that is semi-infinite. The particular solution of the second law equation then takes the form,

\[
c/c_0 = \frac{1}{2} \left[ 1 - \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \right]
\]

where \(c\) is the concentration of radioactive atoms at a distance \(x\) from the diffusion interface after time \(t\); \(c_0\) represents the initial concentration \((t = 0)\) of radioactive atoms in the irradiated half of the composite compact. The error function is tabulated in many mathematical tables\(^{94}\).

This method permits only measurement of diffusion coefficients where \(D\) is the self-diffusion coefficient, when
Fig 28

Sinter I 450 °C

A fraction

5 minutes.
Fig 29

Sinter 1400 °C
A fraction
10 minutes.
Fig 30

Sinter 1350 °C
A fraction
15 minutes.
Sinter 1300 °C
A fraction
20 minutes.
Sinter $1500 \, ^\circ C$

C fraction

30 minutes.
Fig 33

Sinter 1500 °C
C fraction
10 minutes.
Sinter 1450°C
C fraction
10 minutes.

Fig 34
Fig 36

Sinter 1350 °C
C fraction
25 minutes.
there must be an absence of chemical concentration gradients.

Although determination of the cation diffusion rate in an oxide cannot strictly fall within the term self-diffusion it is nevertheless loosely termed as such. This can reasonably be extended to include the field herein undertaken - namely the interdiffusion between two sintered compacts of chromic oxide with minor additions of carbon. The oxides chosen for the study were the fractions A and C - as obtained from batch 2 chromic oxide. The cation diffusion rates in these oxides were calculated from the penetration curves according to the particular solution of Fick's second law. The "A" fraction oxide (+1\% carbon) was investigated over the temperature range 1300°C to 1450°C, Fig.28 to 31; the C fraction oxide (+1\% carbon) from 1300°C to 1500°C, Figs.32 to 37. These temperatures were chosen so that they corresponded to the complementary work on the isothermal sintering of the same fractions. As a confirmatory experiment, the batch 2 oxide was taken and sintered without any carbon addition. This allowed a direct comparison between present and published work on cation diffusivities in chromic oxide, although time prevented the investigation of the activation energy for diffusion in the pure oxide. The interpenetration curve for batch 2
Fig 38

Sinter 1450 °C
Oxide/batch 2
524 minutes.
chromic oxide, without carbon addition, at 1450°C is shown in Fig. 38.

All the penetration curves were symmetrical about the interface, though in the case of the low temperature sintering with little penetration the minimum increment of section (less than one thousandth of an inch) determined the accuracy of location of the interface i.e. $\frac{C}{C_0} = 0.50$. Undoubtedly, the use of more developed experimental techniques would have enabled grinds of the order of ten microns to be made with a correspondingly greater accuracy. The method of cutting can introduce error, since it is paramount that the plane of sectioning be parallel to the diffusion interface. Shirn, Wajda and Huntington have tried to estimate this error but unfortunately their calculations apply only to the particular solution of the Fick's law which includes an exponential term (infinitesimally thin film of isotope on a semi-infinite specimen). Notwithstanding this, they deduce that for an angular error in grinding of one degree between grinder and interface, the error in the slope (log of exponential function) may be 8% ($D = 10^9$, $t = 10^5$, section = $10^{-3}$, c.g.s.).

Liu and Drickamer used a technique similar to the present work - that is the use of grinding paper instead of
\[ \log_{10} T \text{ versus } 10^{-3} \frac{1}{T^0K} \]

**Fig. 39**

Log self-diffusion coefficient \( \text{Cr}^{51} \) in \( \text{Cr}_2\text{O}_3 \) versus reciprocal absolute temperature.

- □ - A fraction.
- ○ - C fraction.

E = 78.1 kmol

E = 76.7 kmol
a precision cutting lathe. It is recognised that the grain size of the emery will give an imprecision to the determination of thickness removed and so a grade was used in this work that was as fine as possible (360A), commensurate with absence of clogging.

The values for the self-diffusion coefficients of chromium in batch 2 chromic oxide, A and C fraction (+ 1/2\% carbon) are shown in the Table below as a function of temperature (calculated from $c/c_0$, and the particular solution of Fick's second law).

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>$D \text{cm}^2\text{sec}^{-1}$ A fraction</th>
<th>$D \text{cm}^2\text{sec}^{-1}$ C fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>$6.15 \times 10^{-8}$</td>
<td>$2.49 \times 10^{-8}$</td>
</tr>
<tr>
<td>1450</td>
<td>$2.21 \times 10^{-8}$</td>
<td>$1.24 \times 10^{-8}$</td>
</tr>
<tr>
<td>1400</td>
<td>$1.08 \times 10^{-8}$</td>
<td>$5.75 \times 10^{-9}$</td>
</tr>
<tr>
<td>1350</td>
<td>$5.41 \times 10^{-9}$</td>
<td>$2.45 \times 10^{-9}$</td>
</tr>
<tr>
<td>1300</td>
<td>$2.70 \times 10^{-9}$</td>
<td>$2.70 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

The value for the self-diffusion coefficient of chromium in chromic oxide batch 2 (without carbon) was calculated from the penetration curve Fig.38 to be $8.10 \times 10^{-10} \text{cm}^2\text{sec}^{-1}$ at 1450°C.

Fig.39 shows a plot of $\log_{10} D$ versus reciprocal absolute temperature; best straight lines were drawn through the log D values for C and A fractions. These resulted in
Fig 40  x20,000

Fig 41  x20,000
activation energies for cation self-diffusion of 78.1 and 76.7 kcal/mole for C and A fraction chromic oxides respectively. It can be seen that the deviation from a straight line is considerable. At high temperatures (1450-1500°C) the cation diffusion appears to be characterised by a higher activation energy in the case of the coarser oxide (C fraction), and to a lesser degree in the finer one (A fraction). The overall activation energy is slightly lower for the higher surface area oxide (A) than for the C fraction oxide.

**Electron Microscopy:**

Figs. 40 and 41 show particle dispersions of the A fraction chromic oxide and the ultrapure oxide batch 4 respectively. It can be seen that there is a strong tendency for the individual particles to agglomerate into clumps. It was this agglomeration that resulted in such difficulty in obtaining a particle size separation by conventional elutriation methods - the separation obtained being a 'pseudo-fraction' of agglomerated particles. At the magnification of x20,000, a particle of one micron diameter would be represented by twenty millimetres linearly on the micrograph. The surface areas of the A fraction oxide and batch 4 give mean particle diameters of 0.277 and 0.124 micron respectively. Though the particles shown on the micrographs are insufficient to be statistically representative of the distribution, it is seen
that the mean sizes are in fair agreement with those obtained by gas sorption methods. There are good grounds for treating the particles as being spherical. This is of course a necessary condition for determining mean diameters from surface area measurements.

Fig. 42 shows an extraction replica x20,000 of batch 2 chromic oxide, sintered at 1400°C for twenty five minutes - without any carbon addition. It was possible to obtain this extraction as the binding of the oxide particles was minimal, allowing the particles to be retained by the Bex film in replication. The Fig. 43, x16,000, shows the same oxide, sintered under the same conditions, but with the loosely retained particles removed by prior application of Bex film. These two pictures illustrate clearly the lack of sintering in oxide without any carbon additions. The linear shrinkage accompanying this sintering time and temperature is indicated in Fig. 19, and is approximately 0.35%. These photomicrographs provide a standard by which to judge the behaviour of sintered chromic oxide with \( \frac{1}{2} \% \) carbon additions.

Batch 2 chromic oxide with \( \frac{1}{2} \% \) carbon admixed was sintered at 1450°C for times of 2, 8, 14 and 20 minutes; the carbon replicas of which yielded the micrographs shown in Fig. 44 to 47 respectively. The corresponding linear
shrinkages are shown in the isothermal sintering curves of Fig. 14, - at twenty minutes the shrinkage being about 9.8% linear.

In all the replicas there was a certain amount of residual Bex film which remained even after prolonged leaching with solvent. It can be seen that the two minute sinter is less complete than the 8, 14 or 20 minute ones. Additionally there was a greater chance of extracting surface particles that were only loosely bound. This further evidenced the lesser state of sintering in the two minute sinter. Extraction occurred only slightly in the case of the 8 minute sinter and not at all in the remainder. Though the structure obtained after about 8 minutes appeared very dense with little porosity, it was possible to observe during the actual scanning of the replica in the electron microscope, areas of voidage where sintering had not occurred. The 20 minute sinter, Fig. 47, showed evidence of grain boundary porosity though this was very finely dispersed.

None of the sinters showed any positive evidence of a reactive grain boundary film. The attempt to etch the grain boundaries selectively (presuming them to contain a higher chromium concentration than the matrix) was also negative.
The likelihood of grain growth having occurred is slight, as a comparison of Fig. 45 and 47 shows. Although the grain in Fig. 47 appear larger than the shorter sinters, this may well be attributable to heterogeneity of the area replicated. At $x_{30,000}$ magnification a particle of one micron will be represented by a linear measurement of 30 millimetres on the photo-micrograph.
DISCUSSION

Throughout this discussion, phenomena relevant to sintering processes in general with their particular significance to the sintering of chromic oxide are considered.

Anomalies between the sintering rates of different oxide batches are examined with reference to possible impurities and particle strain.

The enhanced rates of sintering observed in this work are explained in terms of the stoichiometry shift accompanying the carbon reduction of the normally oxygen excess chromic oxide and the vacancy gradient existing between the neck surface and line of interparticle centres.

Classical sintering models are applied to the initial stages of sintering of the carbon activated chromic oxide. From these are deduced overall rates of diffusion in the activated oxide, which are compared with those obtained for the cation diffusion rates by tracer techniques. The significance of work by other authors on the diffusion rates in plain chromic oxide is also considered.

The deficiencies arising from the application of a classical model to the present system are examined, leading to the proposition of a model for the carbon activated
sintering of chromic oxide.

Definition of Mean Particle Size:

The estimation of mean particle size requires some discussion, since the method used may greatly affect the result. The krypton sorption method employed here will of necessity result in a smaller estimated particle size than that obtained by other means. Flow methods would have tended to measure only a smoothed geometrical area of particle clusters (e.g. Kozeny-Carmen liquid flow method). Confirmation of the sizing was obtained in the case of the C fraction oxide by optical counting which gave a particle size approximately four times that obtained by adsorption methods. Considering that the sorption method measures total available surface, whereas the optical method is limiting for particle sizes of the order of half a micron, there is good agreement between the particle sizes arrived at by the different methods. The electron micrographs of the oxide dispersions indicate that there is little macro-roughness on the particles and that these particles are approximately spherical. The sorption method was therefore used for all the oxides to obtain a mean geometric particle size. Whilst not being absolute, a relative and therefore comparable particle sizing is obtainable for the different oxides studied.
Discrepancies in Sintering Rate between Batches of Oxide:

The slower shrinkage rate of batch 1 chromic oxide may have been due to inter-batch differences in particle size distribution or particle shape, lattice strain or impurity level or species.

In view of the strong dependence of particle size upon the sintering rate it is necessary to eliminate this primary variable when comparing batch behaviour. Fig. 24 shows a plot of linear shrinkage for various oxides versus particle size. Within the relevant temperature ranges, most of the oxides conform to a power law dependence — although the exponent varies with temperature. The exception is oxide batch 1 which exhibits a lower shrinkage rate throughout the temperature range studied. As already mentioned the shrinkage rate is strongly particle size dependent; thus a small error in assessment of the surface area of the oxide, could result in its being wrongly represented graphically. The histogram of the C fraction oxide shows it to have a fairly asymmetric distribution. If the oxide batch 1 had a markedly skewed distribution with a higher proportion of coarse particles of increased surface roughness, it is feasible that the sintering rate was low, the particle size being underestimated because of
the greater surface roughness. It is recognised that particle distribution in itself will affect the sintering rate, and here of course it is not possible to presume in the case of all the different oxides studied. In the case of the two oxide fractions A and C obtained from the same batch 2 one might expect distributions which were asymmetric in the opposite sense if the cut were made about the mean size of the mother batch. That the resulting distributions of the fractions A and C, if not the same, do not affect the shrinkage rate is evidenced by Fig.24, where isothermal points for A, C and batch 2 are collinear.

Residual lattice strain can markedly affect sintering rates. This strain may be induced, among other ways, during chemical preparation of oxides - such as precipitation and calcination - and milling to reduce particle size (Lindley, Ph.D. thesis\textsuperscript{102}).

X-Ray analysis of the chromic oxide batches 1 and 3 for lattice strain revealed no discernable difference between the annealed oxide and the as-received batches.

Thus it seems unlikely that the apparent discrepancy in the sintering rate of batch 1 chromic oxide is due to variation in distribution of particle size or shape or the effect of induced lattice strain during the formative
processes of the oxide.

By elimination of possible variables it remains that disparate impurity effects - significant in all the oxides except batch 1 (or vice versa) - are responsible for the variation in sintering rates. Since there is no single obvious impurity, it is possible only to postulate a general effect of impurities enhancing or inhibiting shrinkages. Batch 1 chromic oxide had a higher impurity level of vanadium than the other oxides. It is possible that owing to the difference between the free energies of formation of vanadium and chromium carbides ($\Delta G^0 = -24.5$ and $-10.9$ kcal/mole of carbon at $1227^\circ$C for VC and $\text{Cr}_3\text{C}_2$ respectively), the lower shrinkage of batch 1 might have been attributed to the formation of vanadium carbide with attendant loss of available carbon, were it not that ample carbon ($\frac{1}{2}$%) was present. The vanadium present at 0.1 wt% in the oxide could account for only about 0.03 wt% of carbon as the carbide VC. Moreover, the quantity of carbon admixed with any of the oxides in no way affects the shrinkage rate within the range $\frac{1}{4}$% to 10% wt.

It is more likely then that the effect - if it is due to the vanadium excess - must in some way be a consequence of the altered ionic mobilities in the sintering oxide.
The higher concentration of vanadium in batch 1 with attendant reduction of available carbon, while not important in the initial sintering stage could be significant during the transition from the power law conformity to cessation of shrinkage. Here - at the transition - it has been shown that the residual carbon in the oxide approaches its minimum value. So, removal of available carbon as vanadium carbide would result in a lower final shrinkage for each sintering isotherm. Reference to the respective isothermal curves of batches 1 and 2 shows no consistent trend as far as differences of plateau shrinkages are concerned (the particle sizes of these two batches were virtually identical).

It thus seems that the shrinkage variation must be attributed to impurity induced disorder in the lattice, the mobilities of the rate controlling ion in the sintering process being decreased in the case of batch 1, or increased in the remaining oxides.

Comparison between Pure Oxide and Activated Sintering:

Since compacts of pure chromic oxide (Lab. Grade purity, particle size ~0.3 micron) show little densification, (See Fig.19 for batch 2 oxide), when sintered to 1400°C for 1000 minutes, it is apparent that the addition of a small quantity of carbon (\(\frac{1}{2}\) wt%) is instrumental in activating the
sintering of the pure oxide. The extent of this effect is such as to achieve a densification of 94% of theoretical by sintering to 1600°C for ten minutes; or comparing linear shrinkages at 1400°C, the pure oxide shrinks 0.31% in ten minutes while the same oxide with \( \frac{1}{2}\)% carbon shrinks 8.32% for the same time and temperature. Although the carbon (of the whisker type, \( \sim 500\) width by \( 1000\) long) cannot be distributed uniformly or spherically on the oxide particle surface, a simple calculation shows that if this were the case (assuming spherical particles, \( 1/10\) micron diameter) then the simple removal of \( \frac{1}{2}\) wt% carbon from the oxide, without any concurrent sintering, would effect a linear shrinkage of about 0.4%. The shrinkage of pure chromic oxide followed a power law, where the time exponent was 0.153; this compares with an exponent of one third for all the oxides sintered with carbon addition.

Philopoulas, Barham and Barrett\(^4\) found that chromic oxide exhibited little dimensional change with time at any temperature (up to 1700°C); this confirmed and extended the work of Clark and White\(^36\). Hagel\(^67\) in a study of the initial sintering of chromic oxide observed linear dimensional changes of 10% after ten minutes at 1200°C, for an oxide of mean particle radius 0.140 micron.
It is surprising that shrinkages of this order of magnitude should have been obtained by Hagel when studying the sintering of ostensibly pure chromic oxide. Not only were high shrinkage rates observed but a power law was obeyed for the initial stages where the time exponent was approximately one half, this indicating a mass transport mechanism to be operative.

The oxide used in the present study with a particle size of this order (diameter = 0.277 micron) is the oxide fraction A. Reference to Fig.15 shows that shrinkages of this order would be obtained only on sintering to 1400°C for this particle size. Fig.24 shows the strong dependence of sintering rate on initial particle size and it can be seen from Fig.17 for batch 3 oxide that at 1250°C a shrinkage of about 10% was obtained. This oxide has a mean particle diameter of 0.155 micron compared with Hagel's oxide of 0.280 micron; it is therefore seen that the initial sintering rate is critically dependent upon particle size. Comparable shrinkages were thus obtained by Hagel and the author at 1250°C for estimated mean particle sizes of 0.280 and only 0.155 micron respectively. The discrepancy could be accounted for by the different techniques for estimating particle size - statistical counting of particle projections (Hagel) and sorption method (present work) - or by impurity differences.
The weight of evidence, including the present work, indicates that plain chromic oxide compacts show little shrinkage at these temperatures (e.g. about 1% at 1700°C, Barrett); though vapour transport is dominant above 1000°C, effecting little shrinkage but increasing the bulk modulus of the oxide. Fig.19 shows the control sintering of pure oxide, batch 2, particle diameter 0.308 micron, at 1400°C, where after 1000 minutes a linear shrinkage of only 0.6% is observed.

The explanation lies probably in Hagel's use of graphite for specimen holders during sintering, and in his use of graphite hot pressing dies in specimen preparation both for tracer analysis (cation diffusion rates) and isothermal sintering.

Work by Stone on diffusion couples showed that the proximity of carbon and oxide was effective in promoting densification over macroscopic distances. It thus seems most likely that the basic system studied by Hagel et al. was not that of pure chromic oxide, but the oxide plus extraneous carbon, which would explain the high densification and the power law time exponent of one half.

Stone has shown that carbon admixtures down to \( \frac{1}{4} \) wt% (lowest studied) were effective in promoting activation, but even with carbon admixtures as low as \( \frac{1}{10} \) wt%, sporadic
shrinkage has been observed by the author.

**Nature of the Carbon Activation:**

As used in this work, the \(\frac{1}{2}\) carbon addition should nominally result in about \(2\frac{1}{2}\) wt\% of the chromic oxide being reduced to chromium (assuming all the carbon is utilised as a reductant and that no carbides are retained). That this reduction of oxide is confined to the particle surface, is a result of the presence initially of the reductant at the surface. It follows then that the very first stage of the high sintering rate must be a consequence of the localised surface disturbance - be this due to defect lattice, vapour, surface or volume transport. This is further evidenced by the fact that initial rates of sintering are unaffected by variation in carbon addition within the range \(\frac{1}{4}\) to \(1\)\%, Fig.10\(^{66}\).

If this were not so it would indicate that the quantity of chromic oxide reduced influenced the shrinkage rate. Since the rate of anion and cation diffusion in the oxide is defined at any temperature, it follows that no stoichiometric disturbance could occur at the particle centre in the initial moments of the isothermal sinterings. Whether or not the ions at the particle centre will diffuse to the surface will depend upon their mobility and the distance to be traversed, i.e. the particle radius.
Effect of Vapour Pressure on Vapour Transport:

Chromic oxide is stable to direct decomposition at temperatures of 1000°C in high vacua of the order of $10^{-6}$ mm Hg. Its vapour pressure is relatively high at temperatures of the order of 1400°C. Caplan and Cohen investigating the mode of volatilization of this oxide concluded that in the range 1000°C to 1200°C, volatilization was confined to oxidising atmospheres when transport occurred via the agency of gaseous chromium trioxide which dissociated to chromic oxide upon redeposition. Vapour transport by this means during the initial stages of surface reduction is therefore very unlikely.

Reference to Fig. 25 shows that the effect of total pressure upon the sintering rate of activated chromic oxide is negligible until a pressure of about $10^{-3}$ mm Hg is reached, above which the sintering rate drops linearly (on a log-log basis). Extrapolation of this curve to one atmosphere results in a hypothetical linear shrinkage of about (2.64) 4.3% which is the approximate maximum shrinkage obtained on sintering the same oxide batch 2 with $\frac{1}{2}$% carbon in an argon stream at the same temperature. This suggests that ambient pressure alone may influence the rate of sintering, apart from any reactivity between the activated
compact and the gas phase. The oxygen potential during the argon sintering (< 2 p.p.m.) was comparable to that which obtained during the vacuum sinterings.

Application of standard free energy principles to the reduction of chromic oxide by carbon, assuming a reaction of the type \( \text{MeO} + 2\text{C} = \text{Me} + 2\text{CO} \), indicates that at 1400°C reduction should proceed if the partial pressure of carbon monoxide is less than one or two atmospheres\(^{100}\). If this condition does not prevail (such as within the oxide compact when initial surface reactions could result in locally high pressures) then the required surface reduction and consequently sintering rate will diminish. Since, thermodynamically, sintering in vacuo is similar to sintering in argon at the same oxygen potential, it must be presumed that the effect of the argon gas is a kinetic one in its inhibition of reaction product removal. It is seen that the sintering rate of chromic oxide and carbon admixtures falls as the total pressure of the system is increased. The extrapolated value of 4% linear shrinkage at one atmosphere presupposes a linear log-log relationship - as shown in Fig.25. Although reduction is still feasible at this pressure it is seen that the shrinkage obtained in an excess oxygen and an argon (oxygen free) atmosphere would be similar. This suggests that the inhibitory effect
in both the vacuum (low pressure air) and argon atmosphere has the same basis, namely a purely kinetic one, the vacuum inhibition being only significant at oxygen and nitrogen pressures approaching that of the argon (i.e. one atmosphere).

Boerickes\textsuperscript{43} considered that reduction occurred via the intermediate step of carbide formation. The presence of a carbide - or any phase differing in lattice type from the matrix - would enhance the propensity of the oxide towards a higher sintering rate - on the grounds that lattice reconstruction would increase the solid state defects in the intervening boundary region; (the intergranular second phase would also inhibit grain growth and therefore preserve the initial grain size).

**Constitutional Effects:**

There is strong evidence that the carbon is merely an intermediary in the production of enhanced lattice mobility, whether this be contained within a surface layer around the particles or penetrating the whole oxide matrix. Analysis of sintered oxide-carbon compacts showed a discrepancy which was consistent with a shift in the stoicheiometry of the oxide (Stone\textsuperscript{66}). Fig.12 shows that at 1400°C up to sintering times of one hour about 0.03% carbon remains in the oxide in an apparently
stable situation. Whether this be as carbide or dissolved in reduced chromium (unlikely as the solubility of carbon in chromium is exceedingly small\textsuperscript{47}) is a matter for conjecture. If the reduced surface layer remains as such and no homogenisation occurs it is possible for there to be a relatively high activity of either carbon or carbide at the surface decreasing towards the centre of the oxide particle. Since the standard free energy of formation of chromic oxide is \(-174.6\) kcal/mole and that of the carbide \(\text{Cr}_3\text{C}_2\) is \(-21.8\) kcal/mole at \(1227^\circ\text{C}\), it is unlikely that the carbide will coexist in quantity with the oxide, unless dissolved in it at very low activity.

**Effect of Activator on Final Shrinkage Value:**

Fig.12 shows that shrinkage virtually ceases when the carbon content of the compact has fallen to its final residual value. It is reasonable to assume that this observation would be applicable to other temperatures and with other batches of oxide.

The possibility that the cessation of shrinkage at \(1400^\circ\text{C}\) of batch 2 oxide is caused by approach to final densification is not supported by the evidence in Fig.14. Here it is seen that at \(1450^\circ\text{C}\) batch 2 chromic oxide achieves a significantly higher shrinkage than at \(1400^\circ\text{C}\) in comparable times. It is then reasonable to suppose that it is the
absence of carbon, responsible for reduction and associated lattice dislocation, that is the cause of the diminution of the shrinkage rate.

Fig. 26 shows the shrinkage rate of batch 2 chromic oxide sintered in dry hydrogen at one atmosphere. Not only does the 'initial' period of sintering conform approximately to the same time exponent of one third (as for chromic oxide and carbon) but the total shrinkage extends far beyond that obtained with carbon activated chromic oxide, (see Fig. 14 and 26). After 250 minutes a shrinkage of about 17% linear was obtained in the case of hydrogen activation.

As is indicated by standard free energy diagrams, at 1100°C hydrogen at one atmosphere will reduce chromic oxide to chromium, if the reaction product (H₂O) is removed to maintain H₂: H₂O > 10³:1, as will pertain during hydrogen atmosphere sintering.

The cessation of shrinkage when the carbon level falls to about 0.03 wt% in the oxide, together with the observation that during hydrogen sintering the shrinkage curve exhibits no plateau, suggest that without the presence of these activators, shrinkage will cease. It is considered that their presence is essential in the promotion of an oxygen deficient lattice, this defect state then being conducive to
the high diffusion and shrinkage rates observed. Of necessity the highest defect density will be located at the particle free surface and neck regions, where removal of the carbon monoxide reaction product (or water in the case of hydrogen sintering), proceeds continuously. A potential difference for a vacancy flux therefore exists from these sources to the particle centre via favourable routes. A mass flux will then be effected in the complementary direction with attendant neck growth and centre to centre approach.

Stoichiometry Shift:

During hydrogen activation, as with carbon activation conditions will again be favourable for the surface reduction of the oxide particles; whether this reduction is carried to completion or merely results in an alteration of the stoichiometry at the surface cannot be definitely ascertained. If a defect structure were to be produced as a consequence of such a reaction, so that the diffusion coefficient of the slower moving ionic species were increased, an increase in the sintering rate (presuming this to be dependent upon the diffusion coefficient) would be expected. In the case of uranium dioxide it is commonly reported that for the oxygen excess \( \text{UO}_2 \text{.14} \), sintering can occur to higher densities than for the more nearly stoichiometric \( \text{UO}_2 \text{.04} \). However tempting
it is to attribute enhanced sintering rates in $\text{UO}_2$, sintered under oxidising conditions, to a defect structure of the oxide, it must be observed that although oxygen diffuses more rapidly in non-stoichiometric $\text{UO}_2$, the oxygen diffusion coefficient is the order of $10^9$ times that of the cation $^{101}$ (at $1600^\circ\text{C}$). Since the uranium is the slower diffusing species, whose rate of diffusion is not oxygen concentration dependent, variation of the oxygen diffusion rate would not be expected to affect the sintering rate.

Thus during the sintering of chromic oxide with either carbon, hydrogen or chromium additions, the cause of the effect of enhanced sintering must be substantially the same - ignoring associated effects such as possible carbide formation in the case of carbon activation.

In the case of carbon activation it is apparent that the carbon, as a source of disorder in the lattice, is not replaced and densification ceases, whereas during hydrogen sintering with a continuously renewable supply and continuous removal of reaction products, the shrinkage is continuous (within the theoretical limits of 100% densification).

Stone had indicated that a permanent stoichiometry shift can occur during the sintering of chromic oxide with carbon and chromium additions, and it is this lattice disorder,
whether confined to the particle surface or not, that is considered significant in enhancing ionic mobilities during sintering. This mobility effect may be additionally enhanced by discrete compound formation where lattice reconstruction occurs (i.e. carbide formation).

Impurity Effects:

Impurities may augment or decrease lattice mobility depending on the impurity. For dilute defect concentrations the electronic conductivity is reasonably assumed to be proportional to the concentration of electrons or holes while the ionic conductivity or diffusion rate is assumed to be proportional to the concentration of ion vacant sites or interstitial ions, in non-stoichiometric disorder\textsuperscript{103}. In impurity induced disorder it is necessary that the impurity concentration exceeds not only the concentration of the intrinsic lattice disorder but also extraneously induced disorder (which obtains in the case of activated chromic oxide), for the diffusion rate to be significantly affected.

Enhancement of Diffusion Processes in the Defect State:

According to the formulation of Zener\textsuperscript{103} for the rate theory of diffusion, the self-diffusion coefficient of an ion by a defect mechanism is directly proportional to the defect concentration.
A decrease in the activation energy for diffusion is a consequence of an increase in the number of solid state defects and departure from stoichiometry (Birchenall).\(^{104}\). A lower apparent activation energy at lower temperature may also arise from preferential diffusion of the ions along short-circuiting paths such as grain boundaries. A study of self-diffusion in alkali halides by Laurent and Bénard\(^{105}\) showed enhanced diffusion along grain boundaries for at least one ion, but with no associated reduction in activation energy. Electrical effects found during the mechanical deformation of ionic crystals containing low angle boundaries suggest that these boundaries are charged\(^{106}\). If the formations of anion and cation vacancies require markedly different energies it is possible that the more easily formed vacancies occupy a fairly broad region on either side of the grain boundary with an associated neutralising charge on the boundary. The preferential diffusion path would then consist of a region of enhanced defect concentration. Enhanced grain boundary diffusion, with a lowering of apparent activation energy has been observed by Oishi and Kingery\(^{12}\) for anion diffusion in aluminium oxide; there is also a low temperature range of sharply lowered activation energy, probably associated with impurity control of defects.
Highly defective compounds have been found to exhibit abnormally high mobility of one component. (Tubandt\textsuperscript{107} studying AgCl and Ag\textsubscript{2}S). Condit and Birchenall\textsuperscript{108} have observed a comparatively low activation energy of 19k-cal/gm-ion for iron self-diffusion in ferrous sulphide with little change in diffusivity from stoichiometric to Fe\textsubscript{0.85}S.

In the spinel oxides the cation mobilities are found to vary markedly from one spinel to the other\textsuperscript{109}. In a single group such as the ferrites the ion mobilities are sometimes very sensitive to moderate changes in the cation composition\textsuperscript{110}. It is fairly certain that the ability of an ion to change valency during a jump process lowers the activation energy and increases the mobility\textsuperscript{104}. It is considered that owing to the strongly reducing conditions prevalent during the activated sintering of chromic oxide, a change of valency from Cr\textsuperscript{3+} to Cr\textsuperscript{2+} occurs, with an attendant enhancement of the cation mobility.

Although cation diffusion is greater than anion diffusion in some spinels such as Fe\textsubscript{3}O\textsubscript{4} it may be lower in others. In the rhombohedral oxides Cr\textsubscript{2}O\textsubscript{3} and Fe\textsubscript{2}O\textsubscript{3} the cations diffuse more rapidly in the former\textsuperscript{72} than in the latter\textsuperscript{111}. It is this difference between the cation
diffusivities in the two oxides that enables a more decisive assessment of the rate controlling ion in the sintering of the oxides to be made. Direct comparison is then possible between apparent diffusion rates and ionic diffusivities as obtained by independent tracer methods.

The foregoing discussion strongly suggests that during the activated sintering of chromic oxide enhancement of the sintering rate is a consequence of the defect state, resulting from the disturbance of stoichiometry initiated at the oxide particle surface. It is unreasonable to suppose the active surface on the particle to be a discrete layer as obtains in the case of the nickel activated sintering of tungsten. As the sintering proceeds the continually renewed defect surface will increase in depth until the whole particle is in a state of increased mobility. The electron micro-graphic work revealed no preferential etching of an active layer for any of the sintering times studied, but this can be explained by the small stoichiometry shift being insufficient to achieve a visibly detectable difference in etching characteristics.

Measurement of the overall energy of activation for ionic self-diffusion during sintering of compacts of different particle size (e.g. "A" and "C" fractions) should
provide an indication of the extent to which an active layer contributes to mass transport and to the sintering process.

1. Regarding Particle as having Active Surface Layer:

   The formulation of Brophy and Wulff\textsuperscript{58} for the possible rate controlling steps during the nickel activated sintering of tungsten is shown in Fig.3. This theory of course presupposes a defined particle surface layer of nickel in which the tungsten is dissolved, and cannot be applied rigidly in the case of activated chromic oxide. Application of the exponents of the dependent variables nevertheless provides an interesting qualitative insight into the sintering process.

   Chromic oxide, it has been found, sinters little below 0.7 Tm. The high shrinkage rates of the carbon containing compacts cannot be accounted for in terms of the known self-diffusion coefficients of chromium and oxygen. An alternative process is that in which the particles are surrounded by a mobile layer (as in the case of tungsten - nickel). During the sintering process where densification occurs a centre to centre approach of particles must be realised, so that it is necessary for the chromium and oxygen ion diffusion to proceed away from the line of particle
centres, through the mobile layer with subsequent redeposition elsewhere on the particle surface. This model is geometrically similar to that proposed by Kingery for liquid phase sintering - the diffusion flux being analagous. In the case of the liquid carrier phase sintering, the driving force is the liquid-vapour surface tension between liquid and pores, and the activity difference existing between the curved surfaces of the neck and particle radius. The basic analysis in defining a rate controlling step was performed in the case of the nickel activated sintering of tungsten in much the same way as Kingery's analysis of liquid-phase sintering.

The first possible rate controlling step is the solution of the oxide matrix into the carrier phase; the second, diffusion of the matrix radially into the carrier phase; the third, the circumferential diffusion in the carrier layer or diffusion circumferentially through the surface layer - matrix interface; and fourth the diffusion radially back to the particle matrix for final redeposition.

The exponents of the dependent variables for each possible rate controlling step are shown in Fig.3 of the literature survey. It must be emphasised that application of this formulation to the activation sintering of chromic oxide is handicapped by the lack of definition of a discrete
carrier phase, the undefined surface layer deepening as sintering proceeds.

Notwithstanding this variation of the surface layer, the qualitative application of the exponents of Fig.3 is revealing. The isothermal sintering curves, in all cases, indicated a law with the time exponent \( s \) close to one third. Shrinkage was independent of activator concentration, (hydrogen partial pressure was not investigated), and hence the appropriate exponent \( n \) is zero. From Fig.24, the gradient of \( \log \frac{\Delta l}{l} \) versus \( \log d \) for \( 1400^\circ C \) is approximately \(-\frac{4}{3}\), whilst at \( 1450^\circ C \) deviation occurs to a lower value. At lower temperatures, the gradient tends to a higher value of exponent. These gradients were consistent in the cases of batches 2, 3 and the fractions \( A \) and \( C \).

These values of \( s, n, \) and \( q \) (namely \( \frac{1}{3}, 0 \) and \(-\frac{4}{3}\)) fit best the rate controlling step \( c \) of Fig.3.

The anomaly in the case of batch 1 chromic oxide has been mentioned previously. Thus, notwithstanding the variation of particle size exponent from the theoretical \(-\frac{4}{3}\), there is a good indication - bearing in mind the limitations of application of a rigid and ideal formulation to a non ideal and variable sintering system - that there exists a mobile layer on the particle, the sintering rate of which
is determined by the mobility of the chromium or oxygen ion species through this circumferential layer.

Since a state of electronic neutrality must prevail, the slower moving ion will be rate controlling in the diffusion controlled sintering process, and it is this ion whose enhanced mobility will effect the activation process.

It is not considered possible by the relationship shown in Fig. 3 to deduce a value for the bulk or surface diffusion coefficient of the controlling ionic type, as the variable $C_0$, the solubility of the matrix in the carrier phase is not sufficiently meaningful in this particular system.

2. Regarding Particle as Uniformly Activated throughout its Mass:

As shown in the literature survey, the models proposed for solid state sintering based on volume diffusion by Coble, and Kingery and Berg et al reduce to the form:

$$\frac{\Delta l}{l_0} = (KD. \gamma \delta^3 t)^m$$

where $K$ and $m$ are constants peculiar to each model. And for grain boundary diffusion:
where \( k \) is Boltzmann's constant, \( D_B \) is the grain boundary diffusion coefficient and "b" the grain boundary width. As already outlined the mobile boundary must be confined initially to the particle surface, and the rate at which the defect state of the surface penetrates the particle will depend upon the diffusion rates of the defects and/or the ion species. It is then not unreasonable to suppose that the disordered surface layer will extend to embrace the whole particle, whose resulting constituent diffusion rates may be considered either in terms of a bulk diffusion \( D_v \) of
enhanced mobility, or of a grain boundary diffusion $D_B$ whose effect is confined not only to a surface layer, but the whole particle. Assuming then that the grain boundary width $b$ extends over one particle radius $r$, elimination of $b$ and $r$ in the foregoing equation leads to the expression

$$\frac{\Delta l}{l_0} = \left(\frac{K D_B \gamma \triangle t}{r^3 kT}\right)^\frac{1}{3}$$

and it is immediately seen that this only differs from the corresponding volume diffusion equation of Coble in the values for the constants, $K$ and $m$; $m$ being $\frac{1}{2}$. It is apparent that the exponent of $r$ is now $-1$ instead of $\frac{4}{3}$ in the case of grain boundary diffusion. One would expect the volume diffusion process - being more significant at high temperatures - to be characterised at higher temperatures by the tendency of the exponent of $r$ to decrease, and this is the case as shown in Fig.24.

The fact that the gradients in Fig.24 show a consistent decrease towards higher temperature can be construed to indicate concurrent grain boundary diffusion and volume diffusion giving way to complete predominance of the bulk diffusion process. To determine a value for the diffusion coefficient of the rate controlling ion, it is necessary to presume it to be constant throughout the duration
of the initial stage of activation sintering, and secondly to estimate a value for $\delta^3$ and $\gamma$ - the volume of compound transported per ion of the rate controlling species, and the surface free energy, respectively. To the author's knowledge no reliable value for the surface free energy is available, but it should not vary greatly from the 1,000 ergs/sq cm used by Coble for $\alpha$-Fe$_2$O$_3$ and $\alpha$-Al$_2$O$_3$. The "vacancy volume" - or more correctly, the volume of compound transported per ion of the rate controlling species - $\delta^3$ is deduced from:

$$\frac{1}{3} \times \text{mole weight} \times \frac{\text{oxide density} \times N}{\text{Avagadro's number}}$$

Taking the density as 5.23 gm/cc, one obtains $\delta^3 = 1.60 \times 10^{-23}$ cc. The factor of one third enters for oxygen as the rate controlling species in the diffusion controlled sintering process; though use of a factor of one half, which would pertain for the cation rate controlling, would not significantly alter the argument.

Application of these values to the sintering equation:

$$\frac{A}{A_0} = \left( \frac{15\delta D_B \cdot \gamma \cdot \delta^3 t}{r^3 kT} \right)^{1/3}$$

for the oxide fractions A and C - activated with carbon addition, reveals an overall diffusion coefficient $D_B$
as a function of temperature:

<table>
<thead>
<tr>
<th>T°C</th>
<th>$D_B, \text{cm}^2\text{sec}^{-1}$, A fraction</th>
<th>$D_B, \text{cm}^2\text{sec}^{-1}$, C fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>-</td>
<td>$6.60 \times 10^{-7}$</td>
</tr>
<tr>
<td>1450</td>
<td>$4.34 \times 10^{-7}$</td>
<td>$3.80 \times 10^{-7}$</td>
</tr>
<tr>
<td>1400</td>
<td>$3.13 \times 10^{-7}$</td>
<td>$1.56 \times 10^{-7}$</td>
</tr>
<tr>
<td>1350</td>
<td>$9.84 \times 10^{-8}$</td>
<td>$3.24 \times 10^{-8}$</td>
</tr>
<tr>
<td>1300</td>
<td>$2.32 \times 10^{-8}$</td>
<td>$6.83 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

A direct comparison is desirable between the values of diffusion coefficients not only between the fractions of differing particle size, but also between activated oxide and unactivated oxide control. However, reference to Fig. 19 for the unactivated oxide sinter shows that although sintering proceeds very slowly according to a power law, the time exponent of 0.153 does not allow application of the Coble type analysis, where time exponents between 0.50 and 0.33 are indicated.

**Tracer Analysis; Comparison with Kinetic Data:**

Nevertheless, an independent determination by tracer of the cation diffusivity in unactivated chromic oxide was made as shown in Fig. 38. Only one determination of this coefficient was made which was at 1450°C, the cation
self-diffusion coefficient being $8.10 \times 10^{-10} \text{cm}^2\text{sec}^{-1}$. This compares favourably with that found by Lindner and Åkerström at 1450°C which was $6.05 \times 10^{-10} \text{cm}^2\text{sec}^{-1}$, but not so well with Hagel and Seybolt who obtained for cation self-diffusion a value of $2.44 \times 10^{-9} \text{cm}^2\text{sec}^{-1}$, for hot pressed chromic oxide.

It can be seen then that the apparent diffusion coefficients of both the A and C fraction activated chromic oxides are by comparison with the tracer values for cation diffusion in pure oxide, of the order of 500 times greater than the unactivated oxide.

Tracer values for anion diffusion in $\text{Cr}_2\text{O}_3$ (Hagel) indicate that at 1450°C a value of $2.21 \times 10^{-12} \text{cm}^2\text{sec}^{-1}$ is representative of the oxygen ion diffusion rate. This suggests that at least in pure chromic oxide, if sintering occurs by a volume transport process, the oxygen ion – being of considerably lower mobility than the cation – is rate controlling.

The high values for the cation diffusion coefficients as deduced from the modified Coble equation, were so great as to justify independent confirmation. This was done in the case of A and C fraction chromic oxide, with carbon activation, by means of the tracer study previously outlined.
<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Apparent diffusivities D̅ from isothermal data, cm² sec⁻¹</th>
<th>Activation energy, E kcal/mole</th>
<th>Cation diffusivities D̅ from tracer analyses cm² sec⁻¹</th>
<th>Activation energy, E kcal/mole</th>
<th>Plain oxide Batch 2, Dcm² sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>-</td>
<td>136.6</td>
<td>139.6</td>
<td>136.6</td>
<td>139.6</td>
</tr>
<tr>
<td>1450</td>
<td>4.34 x 10⁷</td>
<td>2.21 x 10⁸</td>
<td>2.49 x 10⁸</td>
<td>1.08 x 10⁸</td>
<td>1.24 x 10⁸</td>
</tr>
<tr>
<td>1400</td>
<td>3.18 x 10⁷</td>
<td>5.41 x 10⁹</td>
<td>5.75 x 10⁹</td>
<td>5.41 x 10⁹</td>
<td>5.75 x 10⁹</td>
</tr>
<tr>
<td>1350</td>
<td>9.84 x 10⁷</td>
<td>2.70 x 10⁹</td>
<td>2.45 x 10⁹</td>
<td>2.70 x 10⁹</td>
<td>2.45 x 10⁹</td>
</tr>
<tr>
<td>1300</td>
<td>2.32 x 10⁸</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Comparison between Apparent Diffusivities and Cation Diffusivities as Deduced from Isothermal Data and Tracer Techniques Respectively in Carbon Activated Chromic Oxide.

Fig 48
As can be seen from the table, Fig. 48, the cation diffusivities are a couple of orders of magnitude greater than those obtained by Lindner and Åkerström, while the value of Hagel is intermediate. Not only are the diffusion coefficients for the A and C fractions (+ carbon) approximately equal (2.49 x 10^{-8} and 2.21 x 10^{-8} cm^2 sec^{-1} at 1450°C) in the tracer study but the activation energies for diffusion for these two fractions are 76.7 and 78.1 k cal/mole (Figs. 48 and 39). This low activation energy - as opposed to 100 k cal/mole found by Lindner - is an indication that at least the cation diffusion process has been facilitated during the activated sintering stage. Unfortunately no comparison was possible with the activation energy for cation self-diffusion in the pure control oxide, as only one temperature determination was made. However, the low activation energy, combined with the increased cation diffusion rate (tracer), does indicate the strong probability of both anion and cation diffusion enhancement. Since the oxygen ion is of greater ionic radius than the chromium it is likely that the oxygen mobility - though likewise increased - will be rate controlling. That is, unless a situation prevails as in Al_2O_3 where enhanced grain boundary diffusion of the oxygen results in the cation being rate determining.
The values for the apparent overall diffusion coefficients versus temperature, deduced from the isothermal sintering curves - are compared with the cation self-diffusion coefficients from the tracer analysis together with the corresponding activation energies in Fig.48.

If a surface carrier layer only were to exist upon the activated particles, it would be expected that the diffusivities through the compact in the case of the smaller particles (A fraction) with a greater conducting path, would be noticeably higher than those of the C fraction. This is not the case in either the values of the apparent diffusivities from the sintering data or from the cation diffusivities from the tracer studies. In addition to this, the apparent activation energies for the A and C fractions from the sintering data are similar (136.8 and 139 k cal/mole respectively) as are the tracer values for cation diffusion in the two fractions. It is then probable that an active surface layer exists that is confined to the surface during the first few instants of the sintering process only - the resulting state of the whole particle being one of enhanced mobility as a result of the reaction induced disorder.
It is significant that a value of 61,100 cal/mole was obtained by Hagel and Seybolt for the activation energy of cation self-diffusion in chromic oxide. As previously mentioned it was considered that his experimental conditions were such as to facilitate the introduction of trace quantities of carbon into the oxide used for both the tracer and the sintering studies. Granted this, the remarkable similarity between the present work and that of Hagel - both in the values of cation diffusion rates by tracer analysis, and in the form of the isothermal sintering curves, is understandable.

Values found for the anion diffusivities in hot pressed chromic oxide (Hagel) were three to four orders of magnitude smaller than the values for cation diffusion at comparable temperatures, the activation energy for anion self-diffusion being defined at 101 k cal/mole. In view of the lower anionic diffusivity and higher activation energy, he concluded that the sintering process was controlled in the volume diffusion process by the slower moving anion. Values of apparent diffusion coefficients as deduced from initial sintering kinetics - utilising the Coble analysis - were found by Hagel to be consistent with the oxygen ion being rate controlling (within order of magnitude agreement). It can be seen from the table Fig.48, that at any one temperature diffusivities as deduced from tracer analysis and the isothermal sintering
data are compatible within order of magnitude agreement, for
the A and C fractions. It would then follow that the
corresponding rate for anion diffusion in the activated
oxide must be at least of the order of magnitude of that of
the apparent diffusion coefficients of the chromium ion, or
greater.

Confirmation of Oxygen Diffusion Rate in the Activated Oxide:

No independent estimation of the oxygen ion diffusion
rates has been made in the present work, and it would be
necessary to have this information to hand before it could
be categorically stated that the oxygen ions were or were not
rate controlling during the sintering process. However, the
stoichiometric change during the activated sintering process,
implied by Stone's work, favours an explanation in terms of
an enhancement of oxygen ion mobility by virtue of the increase
in oxygen vacant sites.

This effect may be augmented or diminished by impurities
present in the oxide - depending on whether they favour an
increase or decrease in the respective lattice vacant site
concentration. It is not known if these same impurities
would alter the much smaller shrinkage of the plain chromic
oxide. This effect will only become significant when the
impurity concentration is present in such quantities as to
equal at least the effect of intrinsic lattice disorder. Hagel found that one weight percent additions of CeO₂ and Y₂O₃ did not significantly affect the cation mobility - as determined by tracer analysis in chromic oxide.

There is the purely constitutional effect of impurity addition to be considered. It is understandable that the formation of a low melting eutectic film will, at least initially, promote the sintering process by the provision of a mobile surface liquid film, although it is unlikely that constitutional effects could influence the shrinkage rates at temperatures as low as 1050°C, when in the case of the finest oxide (batch 4) chromic oxide, activated sintering was still observed. However, in view of the very high diffusion rates observed throughout this work it is likely that the effect if any will be confined to the initial moments of the activated sintering process, when complete mobilisation of the whole particle has not occurred.

The attendant high rate of chromium ion diffusion observed in the tracer determinations may be explained, in terms of Hättig's²⁹,³⁴ theory of incipient chemical reaction. This can be seen to occur in the case of carbon activation, when enhanced lattice mobility is a consequence of the incipient destruction of the Cr₂O₃ lattice, and lattice reconstruction.
Progressive inward movement of active layer during period of activated sintering.

Grain boundary flux to neck surface.

Centre to centre approach.

Initially unaltered chromic oxide matrix.

Active layer of oxygen deficient non-stoichiometric oxide.

Continuous elimination of oxygen as carbon monoxide from surface during activation.

Enhanced volume diffusion flux of both chromium and oxygen ions in the oxygen deficient oxide layer, to free pore surface and neck.

Fig 49

Schematic Representation of an Intermediate Step During the Carbon Activated Sintering of Chromic Oxide.
Model for Activated Sintering of Chromic Oxide:

Before presenting a schematic model for the carbon activated sintering of chromic oxide, the more significant characteristics not directly explained by classical solid state sintering models are summarised.

1. Shrinkage ceases when the activator concentration approaches a nominal value of 0.03 wt%.

2. The shrinkage process is inhibited on a kinetic basis when removal of the reduction reaction products is prevented, either by the provision of an inert gas atmosphere or by an increase in the oxygen atmosphere partial pressure.

3. High diffusion rates, orders of magnitude greater than those normally encountered in the plain oxide, are observed during activated sintering.

4. A stoichiometry shift is implied from the normally oxygen excess, to oxygen deficient chromic oxide.

It is appropriate to represent the carbon activated sintering of chromic oxide schematically as shown in Fig. 49. It can be seen that to enable a centre to centre approach of the particles to proceed, a volume flux of the chromium and oxygen ions must occur. This diffusion path will occur towards the interparticle neck away from the line between
particle centres, and the unaltered oxide core. It is considered that the elimination of oxygen from the chromic oxide lattice occurs at the free pore surface and inter-particle neck, where the oxygen is removed as carbon monoxide. This surface is consequently a source of lattice defects and disorder, whereas the material at the particle interface and to a greater extent the unaltered oxide is relatively of lower defect density. It is this difference of potential between the neck and pore surface and the particle centre that is, in addition to the normal solid state driving forces, considered the most significant in motivating the enhanced rates of sintering observed in the present work. The cessation of shrinkage when the carbon level drops to 0.03 wt% is seen to be a direct result of the decrease in the vacancy density at the pore surface, the driving potential difference for the mass flux in the complementary direction is then diminished (this does not obtain in the case of hydrogen sintering).

The mass diffusion of the chromium ions is likely to be enhanced in the vicinity of the free pore surface, as a change in valency from Cr$^{3+}$ to Cr$^{2+}$ is probable in the reducing conditions prevailing.
SUMMARY

The initial sintering rate of chromic oxide - carbon compacts (and hydrogen activated compacts of chromic oxide) conformed to a power law where the time exponent was best represented by one third; cessation of the initial rate of shrinkage apparently coinciding with a fall of residual carbon to 0.03 wt%. Hence the high sintering rate was only observed when the activating medium was present.

Severe electrostatic binding of all the oxides occurred during dispersion for microscopical examination, and during the physical separation of batch 2 into fractions.

Linear shrinkage was particle size dependent; when plotted on a linear shrinkage to a constant time versus particle diameter basis, isothermal points between batches were representable by a straight line whose gradient varied from \(-1.09\) at 1450°C, to less than \(-\frac{4}{3}\) at temperatures around 1300°C. Exceptions to this were the ultrapure oxide batch 4 and notably the batch 1 chromic oxide.

The impurity level between oxide batches was found to vary significantly only in the case of batch 1 chromic oxide, which possessed a predominantly higher vanadium level than the remainder of the oxides. Strain, possibly induced
in the oxide particles during their manufacture, was found to be negligible and therefore unimportant when considering inter-batch variation in sintering rates — such as the lower shrinkage rate of batch 1 oxide, this notwithstanding any particle size effect. Impurity level variations between oxide batches are considered unimportant, on a constitutional basis, for the magnitude of impurities found. The exceptional variation of batch 1 chromic oxide activated with carbon, is most likely due to the predominance of impurity induced disorder over intrinsic and activation induced disorder. No study of the effect of impurity level on the sintering of plain oxide batches was conducted.

Interference of the sintering of carbon activated chromic oxide is observed when sintering is conducted in an inert gas atmosphere. This is considered to have a purely kinetic basis, the gas itself presenting a physical barrier to the efflux of gas reaction products from the oxide compact.

Grain growth was found not to occur to a noticeable extent during activated sintering.

The activated sintering process is one in which enhanced diffusion of both the cationic and anionic species occurs;
the cation, whilst not indisputably rate controlling during the activated sintering process, is from the evidence presented, most likely to be so. The introduction of carbon or hydrogen to chromic oxide induces indirectly an increase in the number of oxygen vacant sites, the consequence of which is a greatly increased oxygen ion diffusion rate. Enhancement of the chromium ion diffusion rate is a result of the lattice dislocation and reconstruction accompanying the reduction process (and during the incipient reaction) and probable attendant change in valency from Cr\(^{3+}\) to Cr\(^{2+}\).

The linear shrinkage of the activated oxide is best represented by a hybrid formulation. Diffusion occurs in a mobile layer, which extends as sintering proceeds to produce a completely active particle as a result of the high diffusion rates involved. Cation diffusion rates in plain chromium oxide were within order of magnitude agreement with those found by Lindner\(^{72}\) but were lower than those found by Hagel\(^{69}\) in what was ostensibly pure chromic oxide. The activation energy for cation self-diffusion determined by Cr\(^{51}\) tracer in carbon activated chromic oxide (-77 kcal/gm-ion) compares with Hagel's tracer value for cation diffusion in 'pure' chromic oxide of -61 kcal/gm ion. The disparity between these values and the work of Lindner (activation energy
for cation self-diffusion in chromic oxide (100 kcal/gm ion) is significant. Diffusivities determined from the kinetic curves and tracer analyses for cation diffusion in activated chromic oxide, do not show significant variations between different particle size fractions from the same batch, i.e. A and C fractions from batch 2 chromic oxide. Thus the likelihood of a completely activated particle is indicated during the sintering process; that is, diffusion rates are not a function of the number of conducting paths within the compact.

The sintering of plain chromic oxide did not obey the time law found in the case of carbon or hydrogen activated chromic oxide. Diffusion rates for the cation in plain chromic oxide in the present work were intermediate between those found by Hagel and those of Lindner and Åkerström.

Vapour transport, as an effective means of altering pore shape is unlikely in the case of carbon and hydrogen activated chromic oxide, (this despite its comparatively high vapour pressure). Vapour transport will occur - via the agency of the higher trioxide with subsequent decomposition to the lower oxide on cooling, only in oxidising atmospheres (Caplan and Cohen\textsuperscript{99}), which is not the situation prevailing in the case of carbon or hydrogen activated sintering.
Vapour transport may prevail at least as a means of increasing the bulk modulus in the sintering of plain chromic oxide, when the high vapour pressure is significant without the attendant high diffusivities prevailing during activated sintering.
CONCLUSIONS

The high shrinkage rates of chromic oxide activated with $\frac{1}{2}$ wt% carbon, observed in the present study, are a consequence of the greatly enhanced volume diffusion flux of the component chromium and oxygen ions in an active layer, initially confined to the particle surface. These high diffusion rates are a result of the induced lattice disorder and lattice reconstruction in the non-stoichiometric (oxygen deficient) oxide during the reduction process, by carbon or hydrogen. So long as this activating medium is continually replaced, as in hydrogen activation, the shrinkage is continuous. In the case of carbon activation, shrinkage ceases when the residual carbon level approaches 0.03 wt%. Evidently the function of the activator is both to produce a non-stoichiometric lattice, in which diffusion rates are high, a condition which may continue after the activator is exhausted, and to produce concentration gradients which are the driving forces for directional diffusion. These gradients disappear with activator exhaustion, and sintering virtually ceases. The oxygen-deficient state is not sufficient alone to produce accelerated densification of the degree found in the present work. The sintering data and tracer diffusion rates suggest that it is the chromium ion which is rate controlling during the process of activated sintering.
Activation energies for cation self-diffusion in the activated oxide as determined by tracer analysis, are significantly lower than those reported by Lindner for cation diffusion in plain chromic oxide, though insufficiency low as to indicate a liquid phase mode of sintering.

The rate of shrinkage, and in the case of carbon activation density attained, depends on temperature, strongly on particle size, and on the trace impurities present. Induced particle strain was either insignificant or had no significant effect.

Grain growth was found not to accompany the activated sintering to a noticeable extent.
FURTHER WORK

To reach a final decision relating to the rate controlling step during the activated sintering process, a further study of the oxygen ion mobility is suggested; this could well follow either the accepted tracer techniques for determining oxygen ion diffusion rates by $^{18}$O exchange or autoradiographic methods, though this latter would be restricted to larger particles than those used in the present work.

Elaboration of the present limited study could be pursued for the kinetic and tracer work. Extension of the number of oxide size fractions studied would be desirable - this of course was a limitation of the equipment currently available. The temperature range of the isothermal sintering curves could well be extended - the recording of compact shrinkage being conducted on a continuous basis by means of a Gaertner telescope coupled to a tape puncher or automatic recorder.

The extension would also include a more comprehensive study of impurity effect and pure oxide sintering behaviour. To this end cation diffusivities in plain (and activated) chromic oxide could be determined utilising more refined
sectioning and measuring techniques. Activation energies for cation self-diffusion in plain chromic oxide could then be compared with those of the carbon activated oxide - found herein - and published bibliography, to confirm this present study.
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