A Study of the Sintering of Titanium Powder

by

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This thesis presents a study of some aspects of the powder metallurgy of titanium. With such a reactive metal it is impossible to avoid oxidation and particular emphasis is placed on how oxide films may affect both pressing and sintering. A sensitive, electrical resistance method and dilatometry were chosen to monitor these processes and initial work was carried out on high purity powder. This was produced by the hydride-dehydride process after establishing the conditions required to produce a fine powder which could readily be oxidised. The results obtained from sintering experiments using this material were not suitable for quantitative analysis so a mathematical model was devised to relate resistance change to the processes taking place during the sintering of spherical particles. This model was then tested using simple arrangements of spherical particles.
ACKNOWLEDGEMENTS

This thesis is the result of research carried out at the University of Surrey and AERE Harwell under an AERE bursary. The author is grateful to Staff at these establishments and at ECRC Capenhurst for their encouragement and assistance.
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1. **INTRODUCTION**

With present day concern over the conservation of materials and the efficient use of materials, powder metallurgy is providing an important fabrication route. In its youth, in the 1920's and 1930's, powder metallurgy was used solely for the manufacture of high melting point alloys or to produce components where porosity was an essential property of the product. In the former case, high sintering temperatures or hot pressing had to be resorted to for the removal of the final traces of porosity which, if it had remained, would have reduced the inherent strength of the product and consequently limited the application of powder components. Such treatments have in the last decade been largely supplanted by the processes of sinter forging and extrusion. These processes produce directly a fully dense material having properties which compare well with those of conventionally produced components.

Traditionally, design specifications have been based on the properties of products made by conventional processes. Such properties frequently tend to be superior to those of powder metallurgy components. Today, however, designers realise that powder components will perform satisfactorily and are now able to redefine certain specifications. Both the ability to achieve full density and the modification of design specifications account for the increasing use of powder metallurgy, and an examination of the advantages of this fabrication route indicates applications where it is invaluable.

1.1 **The Advantages of Powder Metallurgy**

The conservation of resources and efficient use of materials have been stated above as reasons for the growth of powder metallurgy and these lead directly to the economic advantages of this process route.
The first advantage is in the reduction of the number of process steps required to make a component. A powder can be compacted directly to the shape of the article required and then sintered to give a strong, dense body. Conventional processes require casting followed by forging, rolling, pressing and machining possibly with reheating at each stage. All these processes add to the cost of fabrication and the more exotic the material, the higher these costs become. For example, titanium requires special refractories and atmospheres which add to process costs.

Secondly, after casting, as much as 25% of the initial cast material may be lost as "flash" and a further 50% may be removed by machining. Using powder metallurgy great dimensional accuracy may be obtained with the minimum weight of material while eliminating flash and minimising machining.

A third economic advantage is that powder can generally be processed at lower temperatures than fully dense material. The sintering of powder particles relies on the reduction in surface energy to bring about densification and a fine powder, having an inherently high surface energy, will become dense at about two thirds of its absolute melting point. Thus, some of the expense of casting may be eliminated. While it is still porous, the powder component may also be more easily deformed than its cast counterpart so there can be some reduction in machining costs. For certain very fine or reactive powders, the advantage of lower operating temperatures may be offset by the expense of handling in inert atmospheres. The economics of providing special atmospheres and glove boxes are considered by White & Smith(2) and Russell(3). However, this may not be such a serious disadvantage as most conventional high temperature processes also require special atmospheres.
An important technological advantage when using powders is the ease of achieving chemical homogeneity. This overcomes the difficulty in producing high quality alloys, such as the superalloys and tool steels, where the conventional casting techniques involve the risk of segregation as a result of density differences of the component metals. Such materials then have to be heavily worked in an attempt to homogenise the structure. Processing may be carried out by mixing the elemental powders or by using pre-alloyed powder where each particle may be considered as a small ingot of the correct composition. Both methods are in commercial use.

Powder metallurgy can also offer special advantages to structural properties. Controlled porosity for filters and bearings has already been mentioned. Grain size can be governed by choice of initial particle size and this in turn influences properties such as the yield stress, the dispersion of a second phase and the magnetic properties of certain materials.

1.2 The Commercial Importance of Titanium Alloys

At this stage a brief discussion of the titanium industry and a few examples of its products will serve to illustrate the importance of powder metallurgy to titanium alloys.

It is now being recognised that titanium has become one of the most significant engineering materials of the past decade. Although volume production is small, two properties, corrosion resistance and high strength-to-weight ratio, make titanium alloys important in the chemical processing and aeronautical industries. Although titanium is the fourth most abundant metal in the earth's crust it is not easily won from the oxide ore because of its stability. It is largely due to the demands of the aircraft industry and the advent of the ICI or the Kroll processes for reduction of...
titanium tetrachloride by sodium or magnesium, that production has
been increased to an industrial scale. Production of sponge by this
method in the United States in 1962 was 6200 tonnes at $3.30/kg, but
the price soon dropped to a level of $2.86/kg. Consumption rose to
18,560 tonnes in 1969, but fell to 12,200 tonnes in 1972 as a result
of the cancellation of several aerospace projects.
Consumption in 1974 had risen to 24,000 tonnes and the sponge price
ranged from $4.50-5.90/kg(4). An increase in the proportion used in
the aircraft industry is predicted after 1975. Consumption figures
for the United Kingdom show a similar trend; a maximum of 2,730 tonnes
in 1969, 2,650 tonnes in 1970 and 1,360 tonnes in 1972, while
production capacity is of 3,000 tonnes per annum(25). Any modest
increase in demand could thus be easily met.
The following table of titanium consumption by various branches of
industry in the USA shows that the aircraft industry is by far the
main consumer despite its decreased demand(4,5).

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<td>Aero engines</td>
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<td>53</td>
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<td>78</td>
<td>56</td>
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<td>Space, missiles</td>
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<td>8</td>
<td>9</td>
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<td>10</td>
<td>13</td>
<td>22</td>
<td>44</td>
<td>38</td>
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<tr>
<td><strong>TOTAL</strong></td>
<td><strong>100%</strong></td>
<td><strong>100%</strong></td>
<td><strong>100%</strong></td>
<td><strong>100%</strong></td>
<td><strong>100%</strong></td>
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(a) predicted

Apart from aeronautical applications, the table shows a steady
increase in the industrial use of titanium. The chemical industry
now uses titanium in the form of sheet and tube in heat exchangers,
for valves and marine structures, such as vats where corrosion resistance is an important factor. Competition in this field against more traditional materials, such as stainless steel and copper, is severe, but long service life and the ability to operate at higher temperatures favour the use of titanium. The high strength-to-weight ratio leads to reductions in centrifugal and inertial stresses in components used at high rotational speeds as in turbines, engines and centrifuges. One minor use is in the fabrication of surgical implants where inertness to attack from body fluids is important. Thus, although the ups and downs of the aircraft industry will determine titanium production in the immediate future, demand from other industries will probably continue to increase as they become more aware of its advantageous properties.

Direct cost comparisons between powder metallurgy and conventional processes are not always easy to make but an attempt can be made in the case of powder forging and conventional forging. Here, the costs of the two processes to make a product of given specification can be compared. For conventional forging, cast titanium ingot may be used at a cost of £4-£7/kg, but with a scrap price reaching £6/kg(6) and assuming waste from flash and machining to be about 50%, the total material costs are likely to be in the region of £10-£12/kg. In the powder forging process, there is little waste in machining, so material costs will fall between the £7 and £10/kg. The latter route has further advantages in that forging temperatures and pressures are lower, thus prolonging tool life and perhaps reducing the number of forging steps.
Thus, depending on powder specification, powder forging could be a cheaper process than conventional forging. If, however, scrap could be used as a starting material for powder manufacture then the cost of alloy powder would be further reduced.

In the aircraft industry, the powder forging process is used in the production of cargo rings and other fasteners using the Ti-6Al-4V alloy. In the case of one aircraft a weight saving of 1,810 kg has been made simply by replacing steel fasteners with this alloy. The same alloy and fabrication route is used to produce guide vanes and turbine blades for engines made by General Electric and Pratt & Witney for the F-15 and TF-39 training aircraft (6, 7, 8).

Another alloy, IMI 685 (Ti-6Al-5Zr-0.5Mo-0.3Si) is used for the compressor blades of the Olympus 593 engine for Concorde and the RB211 engine for the Tristar. This alloy is used for its creep resistance at high temperature. In the case of such titanium-molybdenum alloys, segregation is a hazard during casting so a powder metallurgy route would be advantageous in this case.

Sheet, tube and extrusions such as wire are also produced from titanium alloys. However, widespread application of powder extrusion and powder rolling in the future may make powder metallurgy a serious competitor for the traditional processes. For the time being, maximum cost savings in the production of components are only realised in the case of parts which are pressed and sintered.

When these more recent powder metallurgy techniques are available to industry, it will be possible to process a very wide range of titanium alloys. So far, the most widely used alloy is Ti-6Al-4V (IMI 318). This is a two phase alloy offering through heat treatment a wide range of microstructures and properties. It is already being processed using powder metallurgy. Other alloys have been developed for
corrosion resistance and creep resistance. Thus with mechanical properties which compare favourably with those of steel and with a density of just over half that of steel, it is not surprising that the aircraft industry maintains a high demand for titanium alloys for highly stressed structural parts and engine parts.

In order to illustrate typical mechanical properties of commercial alloys, it is useful to compare in Table 2 two alloys as examples: IMI 130 which is a grade of commercial purity titanium, and IMI 318 which is the two phase titanium-aluminium-vanadium alloy.

Table 2: Properties of Two Commercial Titanium Alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Tensile Strength MN/m²</th>
<th>0.1% Stress MN/m²</th>
<th>Elongation %</th>
<th>Youngs Modulus GN/m²</th>
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<td>IMI 130</td>
<td>460-620</td>
<td>340</td>
<td>20</td>
<td>103-117</td>
</tr>
<tr>
<td>IMI 318</td>
<td>960</td>
<td>880</td>
<td>10</td>
<td>103-117</td>
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</table>

These alloys are already produced in the form of sheet, strip, billet, wire, extrusions and welded tube, which is an indication of the acceptance of titanium as a structural material. As a result of the high cost and handling problems of titanium powder there has been some reservation over its use as a starting material for component manufacture but the high technology aircraft industry is finding its way round these problems and there is now widespread interest in the powder metallurgy of titanium.

1.3 Titanium and Powder Metallurgy

As already shown, titanium is a relatively expensive structural metal and it is evident that a fabrication route using powders would be of great value. To produce parts with good mechanical properties, high density is required and because sintering alone does not produce...
these properties, this is achieved in practice by the forging of powder compacts(6). Normal sintering of titanium powder requires temperatures as high as 1350°C and even then the sintered bodies are not as ductile as the wrought material. This is because of the failure to reach full density and because of the solution of the oxide film on each particle in the matrix. Early work on the powder metallurgy of titanium and zirconium by Hausner(9) and Dodds(10) indicated the significance of oxygen to the properties of a sintered body and emphasised that oxidation should be minimised if useful properties were to be obtained. Although oxidation may be avoided, Norton(11) stated that there will always be a film of titanium dioxide on the powder as it has a large, negative free energy of formation. This oxide may react with more metal during sintering to form the more volatile monoxide which can then evaporate. However, this does not agree with other workers who report an increase in oxygen concentration after sintering.

Kuczynski(12) suggested that oxygen adsorption should increase the sintering rate due to an increase in point defect concentration which activates the process. This is in agreement with his sintering theory but is not supported by experiment as sintering is not enhanced by the presence of oxide film.

Fedorchenko(13) suggested that a non-reducible oxide film, such as that on titanium, can dissolve in the base metal at temperatures below the sintering temperature and will therefore not inhibit sintering. Arensburger(14) compared the sintering of titanium powder prepared by different routes and of different oxygen concentration and sintered for up to 2 hours to achieve near theoretical density in argon at various temperatures. Powder prepared by the calcium hydride reduction route was sintered at 900°C, fine electrolytic powder at 1100-1200°C,
and coarse electrolytic powder at 1200-1300°C. The low temperature
in the first case was attributed to activation of the sintering process
by residual hydrogen, although the actual mechanism was not proposed.
In the other cases, a two stage process was suggested. The first
stage, having a low activation energy, was attributed to solution
of surface oxides while the second stage kinetics suggested a volume
diffusion mechanism. There is therefore some doubt as to the role
of oxide films on the sintering behaviour of titanium powder and it
is intended that this thesis will examine their influence.
An interesting sintering method is described by Boesel et al(15) and
Goetzel and De Marchi(16) who experimented with the Ti-6Al-4V alloy.
Known as spark sintering, the process involves the passing of
alternating and direct currents through the powder compact. The
initial current density is sufficiently large to cause melting at
the contact points between particles. Resistance heating at these
points then causes their growth by the conventional processes.
Densities at 98% theoretical and elongations of 20% were reported,
and an improvement in ductility could be achieved using sodium
reduced sponge or electrolytically prepared powder rather than
magnesium reduced sponge. No attempt was made to study the sintering
kinetics either theoretically or experimentally.
Hohmann(17) investigated the suitability of titanium hydride, titanium
metal and mixtures of the two powders. Under vacuum, and at a given
temperature, titanium hydride sintered to produce a body of greater
density than metal powder produced by the hydride-dehydride (HDDH)
route. This was attributed to the presence of hydrogen which
activated the sintering. However, treatment of the hydride has to be
carried out more carefully to avoid shrinkage cracks during hydriding
although heating to a sufficiently high temperature (1100°C) should eventually weld these cracks together. These powders, sintered at 1100°C under identical conditions, showed slightly different properties; elongation is slightly lower and tensile strength greater for the HDH powder than for metal specimens produced from titanium hydride powder. This is a result of the lower density and higher oxygen content for the HDH material. Analysis showed that about twice as much oxygen was adsorbed in the production of this material. A review of current practice in titanium powder metallurgy has been made by Friedmann(6) and again emphasised the importance of keeping the powder free from oxygen if good mechanical properties are to be obtained but, again, no examination of the sintering mechanisms or the role of oxygen in the sintering process was carried out. However, it can be deduced that the general conditions for the sintering of titanium powder are to use vacuum and temperatures of greater than 1100°C.

It has been stated in this chapter that economic and structural advantages such as the reduction in processing temperature and homogeneity of structure can be achieved using powder metallurgy and these advantages are improved with a fine particle size. However, with such a reactive metal as titanium, the presence of a film of oxide on the particle surface will make a greater contribution to the properties of the material. It is also evident above that little is known about how these oxide films affect the sintering behaviour of titanium powder and it is the intention of this thesis to determine this behaviour.
1.4 Experimental Approach

In order to examine the behaviour of these oxide films during sintering, both experimental method and material have to be carefully selected. As will be seen in Chapter 2, the resistivity of titanium is very sensitive to oxygen content and, in Chapter 6, a model is developed showing the variation of resistance with change in geometry of the contact between spherical powder particles. The changes in contact geometry indicate the sintering mechanism as discussed in Chapter 5, so it is necessary to have a spherical particle shape. Thus the material used in this case was produced at AERE by the centrifugal shot casting (CSC) process.

A parallel study, to simulate a practical sintering application, used a fine powder produced by the hydride-dehydride process. First, suitable conditions had to be established to provide a fine, metal powder having a high surface area to volume ratio. This could then be oxidised to a material having a relatively thick oxide film and high oxygen content. This was then used to examine the effect of oxide film thickness on both compaction and sintering. The resistance measurements were complemented by dilatometry, but the results obtained did not permit an involved quantitative analysis. For this reason interpretation of the role of oxide films on sintering was based on measurements of resistance changes and neck growth of the spherical powder.

2. Properties of Titanium

Before discussing the theoretical and practical aspects of the powder metallurgy of titanium, it is useful to consider briefly some of the physical and chemical properties which are relevant to the work described in this thesis.
2.1 Atomic and Crystal Structure

Titanium has atomic number 22 and is in Group IV A of the periodic table with zirconium, hafnium and thorium. Its atomic weight is 47.90.

$^{48}$Ti is the most abundant isotope and has an electronic configuration of $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$. The ions Ti$^+$, Ti$^{2+}$, Ti$^{3+}$, and Ti$^{4+}$ may occur.

Two allotropes of titanium exist; the low temperature form, α-titanium, has a hexagonal close packed structure with a c/a ratio just less than the ideal value of 1.633, and the high temperature form, β-titanium, having a body centred cubic structure. The transformation temperature is normally given as 882°C.

Several values of the lattice parameters of α-titanium are reported and the most probable values at room temperature, 25°C, are those given by Clarke(18) for iodide refined titanium of fine grain size. Using an X-ray diffractometer the values reported are:

$a = 0.29503$ nm, $c = 0.46831$ nm, and hence the ratio $c/a = 1.587$

The scattering of values found by other authors is attributed to the presence of impurity elements. Clarke(18) and Finlay & Snyder(19) have investigated the effect of common impurity elements in solution on the lattice parameter and their results are presented in the following table.
TABLE 3: The Effect of Small Quantities of Impurity Elements on the Lattice Parameter of α-titanium

<table>
<thead>
<tr>
<th>Addition Element</th>
<th>Parameter Change per Unit Weight Per Cent of Additional Element (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.0</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.2</td>
</tr>
<tr>
<td>Carbon</td>
<td>1.3</td>
</tr>
</tbody>
</table>

The temperature at which lattice parameter measurements are made will contribute to some variation as the mean coefficient of linear expansion of α-titanium at room temperature is $8 \times 10^{-6}^\circ C$ so a temperature variation of $2^\circ C$ will change the last figure of the value by one. From Table 3 it may be seen that the presence of interstitial impurities increases the c/a ratio suggesting that the lowest value of 1.587 is the most accurate as this is the most pure material.

The lattice parameter of β-titanium at $900^\circ C$ is reported by Burgers(20) using X-ray diffraction by a fine wire. The value obtained is 0.332 nm, but the same material in the α-form was found to have the parameters $a = 0.2953$ nm, and $c = 0.4730$ nm, which suggests that this sample was contaminated. Some workers use the quenched and retained β-phase of alloys to estimate the lattice parameter at room temperature by extrapolating values to zero alloy content using the linear expansion coefficient at $900^\circ C$ and ignoring the α→β transformation. In this way, Levinger(21) obtained 0.3283 and Adenstadt(22) the value of 0.329 nm. Similar work by Keller et al(23) using titanium-tantalum alloys yielded 0.329 nm. The most recent determination carried out by Eppelsheimer & Penman(24) gave a value of 0.331 nm at $900^\circ C$ which agrees well with that reported by Burgers & Jacobs(20).
However, this sample was suspected to be contaminated with carbon from its preparation by the magnesium reduction route. All these experiments were carried out on bulk material but for finely divided material such as for powder diffraction, surface contamination becomes more of a problem as X-rays only penetrate the surface layers of material so results must be carefully interpreted if they are then to be used for calculation of the density of pure titanium.

2.2 Density
Using the lattice parameters of iodide refined titanium from the X-ray data of Clarke(18), the density of the α-form is calculated as 4.505 g/cm³. The results of Burgers & Jacobs (20) for β-titanium at 900°C give a density of 4.320 g/cm³.

Again, there may be many higher values to be found in the literature but from the discussion on lattice parameters, it may be observed that oxygen will increase the density as it forms an interstitial solid solution without appreciable lattice distortion. Contamination by interstitial elements can therefore explain the higher density values.

For commercial material the quoted density of IMI 130 is 4.51 g/cm³ and that of IMI 318 (Ti-6Al-4V) is 4.42 g/cm³ (25) both at room temperature. Other than the common interstitials, oxygen, carbon and nitrogen, the chief impurities found in commercial grades are iron, present in many titanium ores, and magnesium or sodium from the reduction process.

2.3 Phase Transformations and Alloying
An approximate value of 882°C for the α ⇌ β transformation temperature is given by De Boer, Burgers & Fast (26) from an investigation of the
resistivity of a titanium wire. Other physical properties also show the allotropic change. The generally accepted value of 882.5°C is from the thermodynamic calculations by McQuillan(27) on the titanium-hydrogen system.

The phase transformation is also extremely sensitive to impurity content. The most common impurity elements, oxygen and nitrogen, increase the stability of the α-phase raising the transformation temperature. According to the titanium-oxygen equilibrium phase diagram published by Hansen(28), oxygen is soluble up to 30 atomic per cent in α-titanium. The maximum solubility in β-titanium is about 6 at. per cent at 1740°C. However, for alloy formation, oxygen and nitrogen are not as effective for hot strengthening as the more widely used α-stabilizer, aluminium. Most high temperature titanium alloys contain aluminium but quantities greater than about 8 wt. per cent tend to order forming the compound Ti₃Al which results in embrittlement of the alloy. An example of a material used in the α-form, IMI 130, has already been given.

β-phase alloys are not used as such at high temperatures because of their poor oxidation resistance and phase instability. β-stabilizers include: zirconium, hafnium and vanadium, which form both α- and β-solid solutions, and niobium, tantalum, molybdenum and chromium. The latter element also forms an intermetallic compound (TiCr₂) in the β-matrix which acts as a grain growth inhibitor during solution treatment. Expense may limit the commercial use of binary alloys because of the large quantities of expensive β-stabilizer required. The most widely used α + β alloy is Ti-6Al-4V.
More complex alloys such as Ti-6Al-6V-2Sn, Ti-13V-11Cr-3Al and Ti-11.5Mo-6Zr-4.5Sn (Beta III) can be used giving high creep resistance up to 300°C making them suitable for fasteners and rivets for supersonic aircraft. Heat treatment can give a fine α-phase dispersion to give high strength. Other features are good cold formability, high fracture toughness and corrosion resistance.

In some alloys such as the stabilised β-alloys described above, the β-phase may decompose on aging to form a metastable omega phase which may cause harmful embrittlement. This ω-phase was first noticed by Frost (29) on an X-ray examination of quenched and aged β-alloys.

According to Williams (30), the crystallography of the omega phase is uncertain but may be compared to that found in zirconium alloys which is described by Douglas (31) as having a hexagonal close packed structure. Ageev & Model (30) state that the lattice parameters of the omega phase in titanium vary with composition but have a fixed c/a ratio of 0.625. This phase is sub-microscopic and richer in titanium than the original β-phase. It appears on aging just before the appearance of the equilibrium α-phase and is thought to be responsible for the high hardness of certain aged alloys. Sargent et al. (32) suggest that with careful choice of alloying elements and heat treatment the harmful effects of omega phase formation can be avoided.

2.4 Melting Point

The melting point of pure, iodide refined titanium is 1668°C, variations from this value again being attributed to impurities, the most common of which carbon, oxygen and nitrogen raise the liquidus. The temperature quoted above is the mean of those determined by Oriani & Jones (33) and Schofield (34) and is widely accepted as...
both experiments used indirect heating methods to minimise contamination and to approach ideal black body conditions. Hansen's phase diagram (28) shows a melting point of 1720°C for pure titanium which is raised by 20°C by 2 wt.% oxygen and involves a peritectic reaction. This high value for the melting point suggests that some contamination has occurred. For comparison, the melting point of commercial purity titanium, IMI 130, is given as 1690°C (25).

2.5 Thermal Expansion

As the lattice of α-titanium is not an ideal close packed structure, a non-linear variation of expansion coefficient with temperature is expected. A table of values is given below.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Temperature, °C</th>
<th>Expansion Coefficient x 10^6/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15</td>
<td>100</td>
</tr>
<tr>
<td>Smitehells (35)</td>
<td>8.35</td>
<td>8.80</td>
</tr>
<tr>
<td>McQuilllan (37)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Williams (39)</td>
<td>-</td>
<td>7.40</td>
</tr>
</tbody>
</table>

Once more there is great variation of values quoted. Smithells (35) quotes the work of Greiner & Ellis (36) but the McQuillans (37) combine this work and that of Fast (38) to produce their values. The material used by Fast is less pure and gives higher values of the expansion coefficient. Greiner & Ellis made measurements in helium using a polycrystalline rod of sintered sponge which had been annealed and cold swaged. These results are compared in table 4 with those of Williams (39) whose measurements are from a rod of commercial grade...
titanium heated in vacuum. These values are slightly higher than those of McQuillan showing the effect of impurities. The grade of material used by Williams is an American grade (A-55) which is similar to IMI 130. Williams also gives values for the β-phase and notes the discontinuity at 882°C indicating the phase transformation.

2.6 Electrical Resistivity
The values of electrical resistivity show a scattering of values attributed to the impurity content of the materials used by various workers. The values obtained by Wasielowski(40) at room temperature for a single crystal are 48.00 μΩ-cm parallel to the a-axis and 45.35 μΩ-cm parallel to the c-axis. The lowest values for polycrystalline iodide rod are 42.00 μΩ-cm measured by White & Wood(41) and Fast(38) and 42.1 μΩ-cm measured by McQuillan(42).

The temperature variation of resistivity is shown in figure 1. It can be seen that up to about 400°C, resistivity increases linearly with temperature, as is expected of most metals, but then begins to increase more slowly with temperature rise. Wyatt(43) shows that the decrease in slope for impure metal is greater than that for iodide titanium and presumes this to be due to the adsorption of oxygen.

The α→β transformation is clearly shown by a drop in resistivity at 882°C and the slope of the curve for β-titanium is small but positive. Greiner & Ellis(36) report the slope to be negative just above the transformation temperature but McQuillan and Wyatt suggest this to be due to impurities which spread the transformation over a wide range of temperatures masking the real transformation temperature.

Jaffee & Campbell(44) have examined the effect of oxygen, nitrogen and hydrogen on the properties of iodide refined titanium and observe a linear increase of room temperature resistivity with oxygen up to
Figure 1  Electrical Resistivity - Titanium
Figure 2. Effect of oxygen, nitrogen and hydrogen on electrical resistivity of iodide titanium at room temperature.
1 atomic percent (see figure 2.). Metal having a nominal zero oxygen content used as starting material had a resistivity of 47.7 μΩ·cm increasing to 55.6 μΩ·cm at 1 atomic percent (0.34 weight percent) oxygen.

Ames & McQuillan(45) and Claissé, Corner & Frigout(46) have both examined the variations of resistivity with temperature and alloy content and have derived expressions to describe the behaviour of such alloys. Claissé et al interpret their observations in terms of the electron-atom ratios. Such a detailed account will not be given here; evidence of the variation of resistivity with temperature and oxygen content is all that is necessary for the work described in later sections.

2.7 Diffusion In Titanium

For the study of oxidation and sintering processes, it is useful to have at hand data for diffusion in titanium. Diffusion coefficients at a given temperature T K may be calculated using the equation:

\[ D_T = D_0 \exp \left( \frac{-Q}{RT} \right) \]

where \( D_0 \) is the frequency factor, \( Q \) the activation energy for the appropriate diffusion process, \( R \) the gas constant.

This equation is sufficient for considering low solute concentrations as shown in the derivations of Lazarus(47) using calculations of the energy of electrons in the lattice and by Swalin(48) using the strain imposed on the lattice by movement of the diffusing atom.

Useful data are given in table 5.
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Diffusing Species</th>
<th>$D_p$ cm²/sec</th>
<th>$Q$ kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>882</td>
<td>Oxygen</td>
<td>1.6</td>
<td>$48 \pm 0.3$</td>
</tr>
<tr>
<td>882</td>
<td>Hydrogen</td>
<td>$5.08 \times 10^{-4}$</td>
<td>33</td>
</tr>
<tr>
<td>700-850</td>
<td></td>
<td>$6.4 \times 10^{-5}$</td>
<td>33</td>
</tr>
<tr>
<td>950-1400</td>
<td></td>
<td>$6.4 \times 10^{-5}$</td>
<td>50.5</td>
</tr>
<tr>
<td>500-825</td>
<td></td>
<td>$1.2 \times 10^{-3}$</td>
<td>50.5</td>
</tr>
<tr>
<td>882</td>
<td></td>
<td>$1.2 \times 10^{-3}$</td>
<td>31</td>
</tr>
<tr>
<td>690-850</td>
<td></td>
<td>$1.2 \times 10^{-3}$</td>
<td>26</td>
</tr>
<tr>
<td>898-1543</td>
<td></td>
<td>$1.2 \times 10^{-3}$</td>
<td>26.4</td>
</tr>
<tr>
<td>700-850</td>
<td></td>
<td>$1.2 \times 10^{-3}$</td>
<td>31.3</td>
</tr>
<tr>
<td>1000-1200</td>
<td></td>
<td>$1.2 \times 10^{-3}$</td>
<td>31.3</td>
</tr>
</tbody>
</table>

Table 5
The data for oxygen diffusion can be used in the following mathematical treatment which deals with the solution of thin oxide films at spherical surfaces.

The kinetics of diffusion are usually given by Fick's second law which is generally stated:

\[
\frac{dc}{dt} = D \frac{d^2 c}{dx^2} \quad \ldots \ldots (2.1)
\]

where \( c \) is concentration, \( t \) is time, and \( x \) is penetration depth.

However, for low solute concentrations this is usually restated as:

\[
\frac{dc}{dt} = D \left( \frac{d^2 c}{dx^2} \right) \quad \ldots \ldots (2.2)
\]

Shewmon (54) derives an equation for the thin film situation where the concentration of solute \( c \) is given by:

\[
c = \frac{\alpha}{2\sqrt{\pi Dt}} \exp \left( -\frac{x^2}{4Dt} \right) \quad \ldots \ldots (2.3)
\]

where \( \alpha \) is the quantity of solute present.

This is a solution of Fick's second law since in the boundary conditions:

\[
x = 0 \quad \text{for} \quad \lim_{t \to 0} c = 0
\]

\[
x \to \infty \quad \text{for} \quad \lim_{t \to \infty} c = C_0
\]

and the total quantity of solute is fixed since:

\[
\int_{-\infty}^{\infty} c(x,t)dx = \alpha \quad \ldots \ldots (2.4)
\]

Crank (55) gives a comprehensive mathematical treatment of diffusion and considers the case of diffusion in a sphere which is of particular interest here if we liken powder particles to spheres. He commences by expressing Fick's second law in a three dimensional form:
\[
\frac{dc}{dt} = \left( \frac{d^2c}{dx^2} + \frac{d^2c}{dy^2} + \frac{d^2c}{dz^2} \right) D \quad \ldots \ldots \ (2.5)
\]

In terms of polar co-ordinates, \( r, \theta, \phi \), then \( x = r \sin \theta \cos \phi, \ y = r \sin \theta \sin \phi \) and \( z = r \cos \phi \) and the above equation may be rewritten considering an element of a sphere of sides, \( dr, r d\theta \) and \( r \sin d\phi \).

\[
\frac{dc}{dt} = \frac{1}{r^2} \left\{ \frac{d}{dr} \left( r^2 \frac{dc}{dr} \right) + \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \frac{D}{\sin \theta} \frac{dc}{d\theta} \right) \right. \\
+ \left. \frac{D}{\sin \theta \sin \phi} \frac{d^2c}{d\phi^2} \right\} \quad \ldots \ldots \ (2.6)
\]

If only radial diffusion is considered, the last two terms become zero and the equation is:

\[
\frac{dc}{dt} = D \left( \frac{d^2c}{dr^2} + \frac{2}{r} \frac{dc}{dr} \right) \quad \ldots \ldots \ (2.7)
\]

Substituting \( u = cr \), this becomes:

\[
\frac{du}{dt} = D \frac{d^2u}{dr^2} \quad \ldots \ldots \ (2.8)
\]

which is the equation for linear flow in one direction. Hence, the radial flow in a sphere may be treated from a linear problem and Shewmon's equation, equation 2.3, for thin film solution may be applied.
2.8 Oxidation

One of the chief problems in the processing of titanium is its great reactivity with the gaseous elements, oxygen, nitrogen and hydrogen. These elements readily penetrate the metal lattice forming solid solutions and embrittling components. Oxidation is the reaction with which we are mainly concerned in the sintering process as, for a fine powder, there is a large surface on which reaction may take place giving unacceptably high oxygen concentrations.

From Hansen's equilibrium diagram (28) one would expect a series of compounds to be formed (figure 3). Recent investigations by French (56) and Japanese (57) authors suggest the presence of the compounds Ti$_6$O and Ti$_3$O, and this has been confirmed by Kornilov & Glasova (58), but are not included in this diagram. In practice, the only oxide of titanium to be formed as a film on the bulk metal below 1000°C is rutile, TiO$_2$. Above this temperature and in the presence of air and water vapour Kinna (59) reports the formation of TiO and Ti$_2$O$_5$.

Many authors give information about the kinetics of oxidation. Ferguson (60) reported that both oxygen anion and titanium cation diffusion occur during oxidation and that oxygen diffusion predominates at low temperatures. A further complication is that titanium ion diffusion predominates at the inner layers of the film and oxygen at the outer surface. This implies growth of the rutile film at the metal-metal oxide interface.

Alexander & Pidgeon (61) have examined the kinetics of oxidation and showed that a logarithmic law is followed at temperatures below 350°C. This was confirmed by Cabrera & Mott (62) who also found a parabolic law to be applicable at high temperatures. Gulbransen & Andrew (64) also
Figure 3. Titanium - Oxygen System
observed parabolic oxidation kinetics above 350°C while Richardson & Grant (50), Davies & Birchenall (65), and Jenkins (66) stated that the parabolic law is followed above 700°C. The last author showed that, for long times, oxygen adsorption becomes a linear function of time.

Hurlen (67) examined the oxidation of sheet titanium in the temperature range 300-700°C at various oxygen pressures and suggests a transition of oxidation behaviour from logarithmic to parabolic at 550°C.

Mindel & Pollack (68) have studied the room temperature oxidation of thin titanium films. During the early stages, oxidation is limited by surface diffusion of oxygen. The later stages are explained by migration of metal vacancies generated at the metal-metal oxide interface. Unless there are large vacancy sinks in the metal, as there would be in bulk metal, a super-saturation of vacancies builds up and opposes further oxidation by reducing the metal activity. This suggests that for thin samples, and this may include powder particles, the oxide film thickness would tend to some maximum value.

This limiting film thickness concept is confirmed by the earlier work of Andreeva (63) who examined the room temperature oxidation of thin films of titanium. On exposure to air, an oxide film of 1.2-1.5 nm thickness is formed. This grows to 5.0 nm following a logarithmic law but then diffusion across the oxide film is reduced so further growth is very slow. Some values of limiting oxide film thickness are given in table 6.

In the case of titanium, the 5.0 nm thick film is responsible for resistance to corrosion. Thicker films are found in certain conditions.
Figure 4. Relationship between oxide film thickness and oxygen content for materials of different surface areas.
Table 6: Limiting oxide-film thickness on several metals oxidised at room temperature

<table>
<thead>
<tr>
<th>Metal</th>
<th>Limiting Film Thickness (nm)</th>
<th>Reference No</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>2.5</td>
<td>51</td>
</tr>
<tr>
<td>Chromium</td>
<td>2.5 - 3.5</td>
<td>63</td>
</tr>
<tr>
<td>Titanium</td>
<td>5.0</td>
<td>63</td>
</tr>
<tr>
<td>Lead</td>
<td>3.1</td>
<td>51</td>
</tr>
<tr>
<td>Aluminium</td>
<td>2.0</td>
<td>51</td>
</tr>
<tr>
<td>Copper</td>
<td>1.0</td>
<td>51</td>
</tr>
</tbody>
</table>

Up to 20 nm, this film is invisible but Flower & Swann (69) have used interference colours to measure film thickness. The first coloured film is yellow at about 40 nm becoming darker until it is blue at a thickness of about 55 nm. Colour can therefore be used as a guide to film thickness. From the above information it can be expected that powder oxidation will be similar to that of thin films and a limiting film thickness will be observed. The only difference in behaviour is that, for a fine powder, there is no means of dissipation of the heat evolved during oxidation. This may result in an increase in temperature which in turn increases the oxidation rate and may result in fire. This pyrophoric nature of fine powder may only be overcome by handling in special atmospheres.

Weight gain is used as a parameter for studying oxidation and this may be related to particle size in the content of a limiting film thickness. If it is assumed as by Russell (3), that the oxide layer is of uniform thickness of x nm, it can be shown that:
\[ x = \frac{W \cdot (M_{\text{aOb}})}{\rho \cdot b_0} \times 10^{10} \]

where \( M_{\text{aOb}} \) and \( b_0 \) are the formula weights of oxide and oxygen, \( \rho \) is the oxide density in g/cm\(^3\), and \( W \) is the weight gain in mg/cm\(^3\). Also:

\[ x = \frac{w \cdot (M_{\text{aOb}})}{\rho \cdot b_0 \cdot S} \]

where \( w \) is the oxygen content in weight present of metal or compound after oxidation to give thickness \( x \), and \( S \) is the surface area of the metal in m\(^2\)/g.

A nomograph (Figure 4) may then be constructed to relate oxide film thickness to oxygen content of the material and its surface area. The information may also be used to determine an equivalent diameter \( d \), assuming a spherical particle where:

\[ d = \frac{b}{\rho \cdot S} \]

Thus, an oxidation study may be used as a method of particle size measurement.

2.9 Summary of Properties

In the context of powder metallurgy, Ogenev et al. (70) reported the oxidation behaviour of titanium powder compacts and found that the rate of oxidation decreased between 800 and 900\(^\circ\)C when most densification takes place. This was attributed to a reduction in surface area due to sintering. Above 1000\(^\circ\)C, densification was slight and oxidation continued following a parabolic law, just as for bulk titanium.
Federchenko(13) and Arensburger(14) suggested that the oxide film on titanium powder dissolved very rapidly between 500 and 550°C, and did not inhibit sintering which begins at a higher temperature. Shewmon's equations confirm this rapid solution. In an example worked by Smith(71) an oxide film of 8.0 nm thickness on bulk titanium dissolves at a temperature of 391°C and an oxygen pressure of 0.2 mPa in 3 milliseconds. If diffusion in a fine powder is more difficult this time may be considerably longer but there is no indication of how this solution of oxygen will affect the sintering process. The work described in this report will clarify this point. The above discussion of properties of titanium may be used as a guide to the expected sintering behaviour and will also aid in an interpretation of the results obtained.

3. POWDER MANUFACTURE

3.1 Purification of Titanium

Metal powders may be produced in a variety of ways of which some will be described below with special reference to their applicability to the manufacture of titanium powder. The methods may be physical or chemical or a combination of both.

A useful precursor for titanium fabrication processes is 'sponge' produced by reduction of titanium tetrachloride either chemically as in the Kroll process, or electrolytically, in a process developed by Cordner & Worner(72). The latter electrolysed a fused mixture of titanium, lithium and potassium chlorides but, because of the low efficiency of the process, it is not commercially viable.
The established commercial purification route is the Kroll process in which titanium tetrachloride is reduced at 900°C by magnesium (or sodium). The resulting magnesium chloride is then leached from the mass leaving titanium as a sponge which may then be broken down by comminution to form powder or melted under vacuum to provide ingots for other manufacturing processes. The chief impurity of magnesium being oxygen and that of the tetrachloride being silicon oxychloride may lead to high oxygen content, typically in the range of 1500-2000 ppm but this may be reduced by vacuum fusion.

High purity titanium may be obtained by dissociation of titanium iodide in the Van Arkel process. In this process impure titanium is reacted with iodine at 500°C to form the volatile tetraiodide. This is then decomposed in vacuum on an electrically heated titanium wire at 1200-1600°C depositing metal on the wire and releasing iodine. The oxygen content of this material is less than 200 ppm. The material resulting directly from this process has no strength for consideration as a structural metal, but provides an essential starting material for scientific investigations.

3.2 Commiution

It has been mentioned above that comminution of sponge is a method of powder production and this is a widely used method. This involves the impact between steel, tungsten carbide or other hard balls and the sponge in this case. Alternatively, metal turnings or some other coarse powder can be used. This method is generally useful for brittle materials or materials which become embrittled by the work hardening which takes place during impact. In the case of soft materials such as pure titanium, variations on the method have to be
adopted to cause embrittlement or to prevent the soft particles being welded together by the impact. Many materials become brittle at low temperature and Dodds(10) reported the ball milling of titanium sponge using a coolant of iced water. Particle sizes of about 70 µm were obtained from which ductile, sintered bodies were made. However, it is likely that the oxygen content of this material is high after reaction with the water. Friedman(6) reported the milling of titanium alloys in a ball mill at -196°C using liquid nitrogen. Although this reduced oxygen contamination, the particles were lamellar in shape and therefore present difficulty in sintering because of inter-particle bridging. For very ductile materials, Arias(73) suggested the use of surfactants which react with the material being milled and prevent the newly formed surfaces from welding together. This technique produces finer powders than if surfactants had not been used. After powder manufacture the surfactant has to be removed. Arias used hydrogen halides as the milling medium and the metal halide surfaces were then cleaned by hydrogen reduction. Work has been carried out at AERE using iodine as a surfactant medium in which to mill titanium. Very fine particles are obtained but these are soft and lamellar in shape and do not sinter easily. The iodine is removed in the early stages of sintering when the iodide dissociates. The disadvantages of the above methods in the case of pure titanium are a combination of the formation of lamellar particles which do not sinter readily and the removal of contaminants from the milling medium. This latter difficulty is another opportunity for contamination by oxidation.
3.3 Fusion Methods

Fusion methods involve the cooling of droplets of molten metal. The simplest of these is the lead shot process but in the case of titanium the molten metal must be kept away from air or water. Thus inert gas atomisation has to be adopted. In this method molten metal is forced through a spray orifice by pressure differential either by inert gas above the metal or by spraying into vacuum. A development of this process is where a stream of molten metal is broken by jets of inert gas as described in the reviews of Klar, Shafer & Gummesson(30). This process is now carried out on a commercial scale and accounts for over half of world powder production. Rough equi-axed particles are obtained with sizes predominantly in the range 10 to 100 μm. For alloys, a well-stirred molten starting material ensures homogeneity of composition and therefore this method is particularly suitable for alloys where segregation is a problem, if conventional casting is used in the fabrication process. However, this method is not suitable for titanium alloys because of their reaction with refractory crucible and orifice materials. The Rotating Electrode Process (REP) has been used by Friedman(6) to produce spherical titanium powders having diameters in the range 30-500μm. In this process a wrought bar of the parent material is rotated about its axis at high speed in a chamber filled with inert gas. The end of the bar, which also acts as an electrode, is melted in an arc and molten droplets are thrown by centrifugal force to freeze in flight as spheres. Friedman reports the production of titanium spheres which are free of major porosity and surface defects and have an oxygen content in the range of 700-900 ppm.
An alternative process is the Centrifugal Shot Casting (CSC) process described by Hodkin et al (74). In this process the feed material, in the form of a consumable cathode, is melted by an arc struck between the electrode and a rotating crucible and is directed towards the chamber walls by centrifugal force. The chamber is filled with inert gas whose thermal conductivity is of importance in determining the shape of particles produced. Argon is often used, but helium having a greater thermal conductivity is used to assist solidification of the droplets before they collide with the wall. This ensures a higher proportion of spherical particles over flakes.

In practice, spherical particles have a limited application. For a given volume, the sphere is the shape having the smallest surface area and hence the smallest surface energy. As it is this energy which provides the driving force for densification, there is thus a limited amount of sintering which can take place and high density is more difficult to achieve than with the rough equi-axed particles, which can also be produced by atomisation. Spherical particles are only of limited application to cold pressing and sintering routes because of low green strength. However, the spherical particles facilitate the control of porosity and are required for a quantitative interpretation of the sintering process.

3.4 Hydride-Dehydride Process

The Hydride-Dehydride (HDD) process may be classified as a comminution method using embrittlement by hydrogen but deserves special mention because of its applicability to the production of titanium and zirconium powders.
Figure 5. Titanium-Hydrogen System.
From the phase diagram produced by Hansen(28), figure 5, it may be seen that the room temperature solubility of hydrogen in α-titanium is very low, while it reaches a maximum solubility of 7.9 atomic percent at 319°C. Excess hydrogen causes the precipitation of the brittle hydride, TiH₂. This may be milled to give a fine particle size. Hydrogen may then be removed by heating in vacuum to leave a metal powder.

Because of the high diffusivity of hydrogen in titanium, the hydride is readily formed at temperatures of about 500°C, and the bulk dimensions of the precursor material only cause a slight difference in times. Therefore, the starting material can be solid bar or, to reduce the reaction time, may be sponge titanium or machine turnings.

The hydriding process has been studied by Antonova & Samsonov(75) and by Tepleenko & Gavrillova(76) who suggest that hydrogen absorption is almost instantaneous at 400°C, and that after 30 minutes at this temperature the hydride formed corresponds to the formula TiH₁.₉₃. Greanspan et al(77) suggest that, in fact, a mixture of titanium metal with hydrogen in solid solution and titanium hydride is formed rather than complete hydride. Hausner(9) studied the hydriding of zirconium at 400°C and at 800°C, and found that at the higher temperature a mixture of the hydride and zirconium containing interstitial hydrogen is formed, and that this requires less milling for a certain particle size than the zirconium hydride produced by the low temperature process.

Hohmann(17) used high hydriding temperatures initially, particularly for titanium alloys or scrap. In the case of alloys, the high temperature is required to dissolve as much hydrogen as possible in the β-phase as complete hydriding is not always possible. In the
Figure 6. Titanium-Hydrogen System. Pressure-Concentration Isotherms.
case of scrap, the high temperature treatment at 650°C under a vacuum of 1.3 to 13 mPa (10^{-5} - 10^{-4} torr) enables surface oxide layers to dissolve so that hydrogen solution is made easier. The hydriding is completed at 450°C. The phase diagram indicates that the maximum temperature for hydriding at atmospheric pressure of hydrogen is 500°C. Above this temperature the hydride is unstable. Milling of the titanium hydride is carried out under argon in a ball mill using tungsten carbide balls to produce fine, about 1 μm diameter, equi-axed particles having rough surfaces. The hydride powder may be sintered after compaction without further treatment; the presence of hydrogen activates the sintering process enabling it to be carried out at lower temperatures. Hohmann has sintered compacts of hydride powder at 1100°C in a vacuum of 1.3 mPa to achieve a relative density of 99%. However, shrinkage is very great and ductility low as a result of the formation of fine shrinkage cracks during dehydrlding. Decomposition of the hydride takes place at elevated temperatures and low pressures. McQuillan (37) has calculated the equilibrium pressure-temperature-concentration behaviour of hydrogen in pure titanium, presented in figure 6, so that the dehydrlding conditions may be chosen to give a known level of residual hydrogen. If a high dehydrlding temperature is chosen, the hydrogen activates the sintering process and leaves a sintered cake rather than a powder. Gavrilova(76) suggested that the use of an anti-sintering agent such as calcium oxide would be beneficial allowing dehydrlding to take place at up to 900°C. The difficulty is then to remove the calcium oxide. An alternative is to use a lower pressure or to remove most of the hydrogen at a low temperature before increasing the temperature to remove the remaining hydrogen. This route offers a convenient process requiring only pure hydrogen
and a high vacuum to produce a powder whose purity then only depends on
the purity of the starting material. It does not rely on sophisticated
apparatus as do the fusion methods and produces equi-axed powder which
has better sinterability than the lamellar powders produced by
 comminution of the metal.

4. CONSOLIDATION OF POWDER

Consolidation is the first stage in making a strong body from powder and in
order to model any process such as sintering in 3-dimensional bodies, it is
necessary to examine the packing and compaction of powders. This can be
affected by the mechanical properties of the metal, chemical bonding,
adhesion and friction between particles and their shape and size. Not all
of these factors are important in this study and some will be neglected.

4.1 Particle Packing

For simplicity, the first case of 3-dimensional packing to be
considered is a simple cubic array of spherical particles. A unit cell
of 8 spheres, each of radius $R$ can be packed into a cubic box of side $L$.
The volume of the spheres is $8 \times \frac{4}{3} \pi R^3$ and that of the box is $64R$
units. The ratio of these values gives the porosity which in this case
is 47.6% of the total volume. In another arrangement the spheres may be
staggered, those of one layer resting in the interstices of the layer
below this reducing porosity relative to that of the simple cubic array
above. Fraser (78) has calculated the specific porosities for several
arrays as shown in table 7.

<table>
<thead>
<tr>
<th>Type of Packing</th>
<th>Maximum Porosity (%)</th>
<th>Coordination Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple cubic</td>
<td>47.6</td>
<td>6</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>39.5</td>
<td></td>
</tr>
<tr>
<td>Body centred cubic (BCC)</td>
<td>32.0</td>
<td>8</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>30.2</td>
<td></td>
</tr>
<tr>
<td>Pyramidal, face centred cubic (FCC)</td>
<td>26.0</td>
<td>12</td>
</tr>
<tr>
<td>or Hexagonal close packed (HCP)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
However, when spheres are packed into a container they do not immediately take up the most dense arrangement and this can complicate any attempt to model the process of compaction. Vibration can greatly increase the density of a haphazard arrangement of spheres from about 54% to between 60 and 70%. Bernal (79) studied the packing of spheres in his examination of the structure of monatomic liquids and found the value of closest random packing density after vibration to be 64%, compared with 60% for loose packing and 74% for close packing. He concluded that this random close packed array would have a statistical co-ordination number of 8 if the spheres' centres were within 1.05 diameters of one another. These values of packing density and co-ordination number approximate to those of the body centred cubic structure, and it may be possible to use such an array for a model of the sintering process. Besides vibration, another method of increasing the density is to fill the interstices between spheres with smaller spheres. Indeed, commercial powders generally have a range of particle sizes and vibration is not always necessary to increase density. In an ideal tetragonal lattice of spheres of radius R, the interstices may be filled with spheres of radius 0.414 R reducing the porosity from 30% to 20%. Brown (80) carried out work using atomised steel powder of 12 sieve fractions. By making binary mixes and vibrating the mixture he found a maximum density was achieved when the ratio of primary to secondary sphere diameters was about 6. Ternary mixtures were less critical in composition and a porosity of 33% was generally obtained. Particle shape can also affect compaction. For example, particles of cubic shape should pack to zero porosity, but Fraser (78) showed that
a haphazard arrangement yielded a porosity of 20-35%. A value of 10% was obtained for discs or cylinders. Some powder manufacturing processes produce plate-shaped particles, which tend to form bridges and make compaction more difficult. Moon(81) considered that irregularly shaped particles have a greater packing efficiency as the particle shape deviates from spherical. This he attributed to the asphericities of some particles fitting into the interstices of groups of particles as they re-orientate on vibration. This would make it more difficult for the infiltration of fine, irregularly shaped particles when making a binary mix, so a high uniform packing density would become more difficult to obtain. Hausner(82) demonstrated that the tap density of irregularly shaped copper particles was only 60% of that of spherical particles of the same size showing disagreement with Moon. However, a uniform density could be achieved which is important for the properties of a sintered body. Schelner(83) and McLaren & Atkinson(84) have found that oxide films reduce the friction of metal powders and hence increase their tap densities. The latter authors found that a weight gain of 0.39% due to absorbed oxygen increased the green density of uranium nitride by 2%. A similar observation has been made by Turba(85) on barite where adsorbed gas and water layers act as lubricant. No quantitative information exists for the lubricating effect of oxide films on titanium powders. However, for bulk titanium Machlin & Yankee(86) found that the static friction coefficient decreases from 1.15 to 0.70 when the oxygen content is increased to 0.2 weight per cent. After heating bulk titanium in air at 350°C for 17 hours the friction coefficient between copper and titanium decreased from 0.63 to 0.25. Although these values apply to bulk material, it may be assumed that the reduction of friction coefficient is due to the presence of surface
oxides. So for powders, oxidation may assist movement of particles over one another and allow greater densities to be obtained on compaction.

4.2 Particle Compaction

During compaction of powder arrays, three processes may be considered to occur. First, particles slip over one another so that they become stacked more efficiently in the die. This is affected by the friction forces between the particles and the process is stopped when particles become locked in position or form 'bridges' around large pores. In the second stage, elastic compression takes place at the contact points between particles resulting in an increased area of contact. This stage has been examined theoretically by Hertz(87) and by Easterling & Tholen(88), who derive expressions showing that the cube of the contact diameter is inversely proportional to the Youngs Modulus of the material. This stage of compaction is relatively unimportant for fine particles as, for small contact areas, the elastic limit is exceeded by very small pressing loads and the final stage of compaction is reached.

In this third stage, plastic deformation takes place giving an increase in contact area and a permanent decrease in porosity. For brittle materials, this stage is not reached and particle fragmentation occurs. The third stage of compaction has been considered in detail by Pelzel(89), who examined the changes in geometry of spheres stacked in two sample arrays: simple cubic and face-centred cubic. He derived the changes in contact area and porosity as the spheres deform plastically, and good agreement between theory and practice was obtained for copper and iron powders, particularly at low pressures.
before work hardening took place. At high pressures, the interaction between powder and die wall must not be neglected as compaction deviates from isostatic behaviour.

In practice, qualitative analysis of powder compaction is difficult as there is rarely any ordered stacking of particles which may be assumed. However, a simple mathematical treatment can be applied. Many authors use the relationship between compaction pressure and volume or density to quantify the process. Donachie & Burr (90) and Morgan & Sands (91) respectively examined copper and sponge iron powder, and plotted the logarithm of compaction pressure versus relative void content and produced curves having three distinct gradients, presumably corresponding to the three densification mechanisms discussed above.

The most recent numerical analyses of powder compaction have been carried out by Kawakita (92) and Bockstiegel (93) using the probability of void volume decreases and the elastic and plastic behaviour of the material to arrive at a general compaction formula. The details of this treatment will be omitted here as the formula may be simplified as indicated by James (94), so that a linear relationship exists between the logarithm of porosity or volume change and the compaction pressure, and this simple treatment will be used later.

From the above, it can be seen that the compaction behaviour of powders can be treated very simply for comparison of different types of powder, e.g. oxidised and unoxidised powder. The particle arrangements for random arrays of spheres may approximate to an orthorhombic or body-centred tetragonal array if packing density and co-ordination number alone are considered, and this will be of use in an attempt...
to model the resistance of an array of spheres in order to examine their sintering behaviour.

5. THEORIES OF SINTERING

Powders differ from solid, polycrystalline material in that they possess a large ratio of surface area to volume and, hence, a large amount of surface energy. It is the reduction of this energy which is the driving force for sintering. This energy and thus the driving force will be greater for finer powders, so it is advantageous to be able to handle fine powders. Time and temperature play a role. As sintering proceeds, the energy available is reduced and the sintering process is slowed down. At high temperature atomic movement is easier and sintering is promoted.

On the macroscopic scale, four important stages may be distinguished during the sintering of a powder agglomerate to produce a dense body. The first stage, Stage 0, recently proposed by Behar et al. (95) is that in which slight particle movement takes place to allow contact between particles. This is a result of incomplete compaction so that particle movement is possible. It is observed particularly with spherical powders having smooth surfaces and those compacted at low pressures. This stage is therefore only observed in a limited number of cases.

The second stage, Stage I, is most widely reported and involves the initial neck growth at the contacts between particles. The particles retain their individuality and only a small amount of shrinkage, about 5% takes place.

The intermediate stage, Stage II, involves densification and grain growth may begin. Most shrinkage, up to 90%, takes place during this stage in which the pores which remain interconnected become cylindrical in shape.
The final stage, Stage III, is reached when the pores become isolated and approximately spherical in shape. At this point, the last 10% of porosity is only slowly reduced because further densification is hampered by diffusion over long paths to grain boundaries, and the slow kinetics of the removal of gas which may be trapped in the pores.

In practice, there is a clear distinction between these four stages and between the mechanisms taking place. Many attempts have been made to quantify the sintering process in order to establish the mechanisms responsible. In order to examine these mechanisms and consider their respective limitations and contributions to the sintering process, it will be necessary to refer to figure 7 for the particle geometry. For simplification, it will be assumed that particles are spherical.

The mechanisms responsible for sintering are:

- Evaporation and Condensation: does not produce shrinkage but may account for neck formation and spheroidising of pores.
- Volume Diffusion from grain boundaries or dislocations to the neck causing shrinkage and neck growth.
- Grain Boundary Diffusion which accounts for shrinkage and neck growth.
- Surface diffusion which assists neck growth and pore spheroidising but does not contribute to shrinkage.
- Viscous or Plastic flow which involves dislocation movement and the relief of stress at contact points.

These mechanisms will now be discussed in more detail.
Figure 7: Neck Geometry of Adjacent Spheres

Figure 7(a): No shrinkage  Figure 7(b): Shrinkage occurs

Neck curvature: $\rho = \frac{x^2}{2a}$  $\frac{x^2}{4a}$

Neck area: $A = \frac{\pi x^3}{a}$  $\frac{\pi x^3}{2a}$

Neck volume: $V = \frac{\pi x^4}{2a}$

Curvature difference: $K = \frac{(1 - \frac{1}{\rho}) + \frac{2}{a}(1 - x)}{a} = \frac{\frac{1}{\rho} - \frac{1}{x}}{a}$
5.1 Evaporation and Condensation

Material transport in the vapour phase is important in a limited number of cases where the material is at sufficiently high temperature for its vapour pressure to be appreciable. It does not contribute to shrinkage but only to pore spheroidisation and neck growth so it cannot be neglected.

At a curved surface, the vapour pressure of the metal depends on the radius of curvature according to a Gibbs relationship.

\[
\ln \frac{P_1}{P_0} = \frac{\sigma M K}{d k T}
\]

where \(P_1\) and \(P_0\) are the respective vapour pressures over curved and flat surfaces, \(\sigma\) the surface energy, \(d\) the density, \(k\) the Boltzmann constant, \(T\) the absolute temperature, \(M\) the molecular weight, \(K\) is described in figure 7(a). By definition, the vapour pressure is negative over a concave surface, the neck, and positive over a convex surface, the sphere. Thus, there is a pressure difference which provides a driving force for material transport.

The rate of transport of material may be expressed in terms of the rate of volume change \(\frac{dV}{dt}\) at the neck between two spheres:

\[
\frac{mA}{d} = \frac{dV}{dt}
\]

where \(m\) is the rate of condensation per unit area of vapour given by:

\[
m = \frac{\Delta p (\frac{M}{2})^{\frac{1}{2}}}{2\pi k T}
\]

\[
\text{43...}/
\]
If the pressure difference $\Delta p = P_o - P$ is small, and $x << a$
then: \[ \frac{\Delta p}{P_o} = \frac{x}{a} \quad \text{and equation (5.1) becomes:} \]

\[ \Delta p = \frac{\gamma M_P}{d P_o} \frac{\rho}{kT} \quad \ldots \quad (5.4) \]

Substitution for $m$ in 5.2 and using the geometric approximations of figure 7(a), we have:

\[ \frac{x}{a} = K, \quad \ldots \quad (5.5) \]

where $K$ is a constant.

This is the equation first proposed by Kuczynski(96). Consideration of the geometry changes during this process show that material evaporates only at free convex surfaces and condenses at concave surfaces such as the neck. Thus, the distance between particle centres is unaffected and shrinkage cannot be explained by this mechanism.

5.2 Plastic Flow

In this mechanism, it is assumed that stresses exist as a result of surface curvature: tensile stresses in the neck and compressive stresses on the convex surface of the particle. If compressive stresses are defined as having positive value, then the stress at the neck circumference is:

\[ \sigma_x = \frac{\gamma (1 - \frac{1}{r})}{x} \quad \ldots \quad (5.6) \]

There is also a stress gradient on the grain boundary of the neck as by symmetry, stress at the neck axis is zero. At high sintering
temperatures, the stress can be sufficiently high to cause plastic flow in the neck region. Three mechanisms are generally considered responsible for plastic flow: Nabarro-Herring creep, viscous flow, and creep by dislocation motion.

5.2.1. Nabarro-Herring Creep
This mechanism proceeds by diffusion of vacancies from areas of high chemical potential to areas of lower potential and is thus similar to volume diffusion which will be described below.

5.2.2. Viscous Flow
This mechanism is usually considered for the sintering of glasses and some polymeric materials. An expression for the rate of neck growth in terms of the viscosity coefficient has been deduced by Frenkel(97) but the mechanism is not considered to be significant in the sintering of metals.

5.2.3. Dislocation Motion
In recent years there has been much argument over the role of dislocation motion as a sintering mechanism. Of those authors who consider plastic deformation important, Kuczynski(96), Lenel & Ansell(98) and Johnson(99) concede that it is only important in the early stages of sintering.

Kuczynski's analysis has been elaborated by Moore(100) who showed that the initial shrinkage rate assuming plastic flow is greater than that possible by diffusion from the grain boundary. However, the plastic flow contribution soon becomes insignificant.

A more practical approach to the sintering of cold pressed powders was adopted by Easterling(101). Pressing deforms the contact points between particles introducing a high local dislocation density. The
deformation accounts for neck formation and growth is then possible by dislocations moving to areas of lower chemical potential such as the grain boundary. This is demonstrated in a computer model by the same author\textsuperscript{102} in which chemical potential maps have been produced. It was found that only dislocations within about one neck radius of the neck are influenced by forces great enough to move them. Outside that zone the chemical potential gradient is too small to cause them to move. This is confirmed by electron microscope studies of several types of spherical metal powders. The maximum shear stress at the neck is also never high enough in practice to nucleate new dislocations and maintain the gradient. Thus, creep processes in which dislocation climb is necessary, cannot take place. As the dislocations rapidly move to sinks, this mechanism is completed in the early stages of sintering and contributes little to shrinkage.

In agreement, Torkar & Perlhefter\textsuperscript{103} deduced that deformation stresses are eliminated at temperatures lower than those at which densification takes place and are of no practical importance.

Lenel\textsuperscript{104} emphasised the significance of plastic flow in later work. He postulated that in the early stages of sintering, the radius of curvature of the neck is small so stress due to surface tension is high allowing material transport by dislocation motion. As the necks grow their radius increases, and the stress decreases reducing the driving force for dislocation motion. Further sintering must then take place by one of the diffusion mechanisms.

Experiments have been devised to show the importance of the plastic flow mechanism. A dispersion of alumina markers in silver wires which have then been sintered at 935°C suggests the validity of Lenel's work. If material is transported by surface diffusion, there will be...
no movement of markers into the neck region as atom or vacancy movement could not move the markers. If transport is by diffusion using the grain boundary as a sink, only the centre of the neck will contain markers and there will be marker-free zones where material is deposited. If dislocation motion is responsible then the distribution of markers will be unchanged. The latter was observed by Lenel(104). However, in this case, it is possible that dislocations are nucleated at the markers which would tend to favour this mechanism for such a composite material while, for pure silver particles, this mechanism may be negligible. In fact, Johnson(110) regards grain boundary and volume diffusion as predominant for silver at 900°C. Lenel derived the rate law for neck growth by dislocation movement as:

\[ \frac{x^9}{a^{4.5}} = K_2^t \]  

(5.7)

Experimental work also predicted the value of \( x/a \) for which plastic flow and diffusion contribute equally to the shrinkage of silver powders and hence the point at which transition from one mechanism to the other will occur. Lenel also stated that until diffusion took place, the stresses in the particle would be sufficient to create new dislocations. Although the evidence of dislocation movement is indirect, measurement of \( x/a \) agree with the predicted rate law confirming that a plastic flow mechanism was responsible in this case.

5.3 Diffusion Mechanisms

The early equations for sintering by diffusion assume a gradient of vacancy concentration which is then reduced to the equilibrium vacancy concentration throughout the material by the driving force of surface curvature. Modern theory assumes an equilibrium vacancy
concentration already exists and that neck growth is by atomic diffusion under the influence of surface curvature difference. However, both the vacancy flux and atomic flow equations lead to similar equations for neck growth. The change in vacancy or atom concentration, $\Delta c$, at the neck is then related to the rate of volume change at the neck and the diffusion coefficient:

$$\frac{A\Delta c}{p} \frac{dV}{dt} \ldots \ldots (5.8)$$

$D'$ is the appropriate diffusion coefficient, $D_b$, $D_v$, or $D_s$, depending on whether grain boundary, volume or surface diffusion is the mechanism operating. The appropriate geometric approximations of figure 7 are then substituted in the above equation which is then integrated to obtain an equation describing the neck growth kinetics for the mechanism which is assumed to be operating.

For example, in the case of volume diffusion, the approximations of figure 7(b) are used for which Kuczynski(96) obtained the equation:

$$\frac{X^5}{a^2} = 40 \frac{8\delta^3}{K} \frac{D V}{t} \ldots \ldots (5.9)$$

where $\delta$ is the surface energy, $\delta$ the atomic volume, and $t$ is time. Johnson & Cutler(105) derived the same equation for volume diffusion with the grain boundary acting as a vacancy sink except the right hand side is 8 times greater. They also expressed their geometric approximations in terms of shrinkage, $\Delta L/L_o$, to obtain equations for the sintering kinetics of a line of spheres. For example, the volume diffusion mechanism yields the equation:

$$\frac{\Delta L}{L_o} = (K \frac{8\delta^3}{K} \frac{D V}{\delta^2}) 0.46 0.46$$

$$\frac{1}{K} \frac{8\delta^3}{K} \frac{D V}{\delta^2} t \ldots \ldots (5.10)$$

48...
The two types of equation may be written as:

\[ x^w = \frac{K \alpha^3 D a^s t}{kT} \]  \hspace{1cm} \ldots \ldots (5.11) \]

\[ \frac{\Delta L}{L_0} = \left( \frac{K \alpha^3 D a^p}{kT} \right)^n \]  \hspace{1cm} \ldots \ldots (5.12) \]

The values of the constants, \( K, K^1 \) and of the exponents \( w, s, p, m \), found by various authors are presented in Table 8.

<table>
<thead>
<tr>
<th>Author</th>
<th>Diffusion Path</th>
<th>Eq (5.11)</th>
<th>Eq (5.12)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( K^1 )</td>
<td>( K )</td>
</tr>
<tr>
<td>Johnson &amp; Cutler (105)</td>
<td>Lattice</td>
<td>43</td>
<td>31/( \pi )</td>
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<td></td>
<td>Grain boundary</td>
<td>115b</td>
<td>505/7( \pi )</td>
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<tr>
<td>Kingery &amp; Berg (106)</td>
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<td>20/( \sqrt{2} )</td>
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<td></td>
<td></td>
<td>5</td>
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<td></td>
<td>Grain boundary</td>
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<td>15( \alpha )</td>
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</table>

..../
Table 8 shows general agreement between several authors for the values of the exponents for the respective mechanisms. The equations of Johnson & Cutler are widely accepted as their geometric approximations allow for changes in particle radius. However, during the initial stages of sintering, this radius may be constant, so measurement of the neck radius can be used to determine the sintering mechanism as a plot of log x or log x/a versus log (time) will give a line of slope 1/w.

Experimental work by Kuczynski using copper spheres sintered between 500 and 800°C, and using silver spheres between 700 and 900°C, gave a line of slope 1/5 suggesting lattice diffusion to be the dominant mechanism in disagreement with Lenel's results which suggested a plastic flow mechanism. Coble's model predicted a slope of 1/4 for the lattice diffusion mechanism but his experimental work on alumina powder gave a value of 1/5 agreeing with the other authors.

From the table, it may be noted that Johnson's(105) equation for grain boundary diffusion has the same exponents as would be expected for surface diffusion. To distinguish between these two mechanisms neck growth measurement must be supplemented by shrinkage measurement. Grain boundary diffusion will result in shrinkage of the compact whereas surface diffusion cannot account for shrinkage.

All the derivations used to produce equations 5.11 and 5.12 make the assumption that a single sintering mechanism is operating. In practice, it is generally agreed that sintering occurs by a combination of mechanisms, which may operate simultaneously. Johnson(99) has considered the sintering kinetics when grain boundary diffusion and volume diffusion from the grain boundary contribute...
equally to shrinkage. More complicated geometric approximations than those of figure 7 are required and the equations are therefore limited to about 3.5% of shrinkage. The contribution of other mechanisms to shrinkage is assumed to be negligible. The constants and exponents for these equations are also tabulated. Johnson's derivations differ from those of Coble and Rockland in that they assumed that a gradient of vacancy concentration was responsible for diffusion while Johnson considers atom migration under the influence of surface curvature. Johnson suggested that a vacancy mechanism could not account for the sintering of doped ionic compounds(99,109). Kingery & Berg(106) used a flux equation which is valid only for volume diffusion from the sphere surface to the neck and neglects any diffusion from the grain boundary to the neck. However, in most cases, the grain boundary is at the neck and the two contribute simultaneously. These sintering equations must therefore be used with caution. If reliable shrinkage and neck growth data are available it is possible to obtain the exponent, which will then define the sintering mechanism, and the diffusion coefficient. Johnson(110) has studied the sintering of silver powder at 900°C and the exponents obtained suggest that sintering occurs by grain boundary diffusion with a minor contribution by volume diffusion. From his data, diffusion coefficients were calculated which agree well with other published values.

The simultaneous operation of several sintering mechanisms has been considered by Ashby(111) who used diffusion data to predict by calculation, which sintering mechanism is predominant under given conditions. He equated pairs of simple neck growth equations so that at a given temperature, the neck size could be calculated if the
two mechanisms gave an equal contribution to growth. He thus produced maps which indicated the predominant mechanism. This method relies on the existence of reliable diffusion data and as only the simple sintering equations are used, the method can only be applied to about the first 5% of shrinkage beyond which these equations are no longer valid.

A further limitation of the above equations is that they all relate to spheres of a single size and this is recognised by Coble(112). He considered the effects of particle size distribution and concluded that, during the initial stages of sintering, the sintering rate would be intermediate between those predicted for the end-member sizes. Thus an effective particle size could be used for application of the sintering equations. Thus, it is possible to measure neck growth rate and obtain an exponent to predict the possible sintering mechanism subject to the usual limitation of the sintering equations being applicable to the first few percent of shrinkage.

5.4 Intermediate and Final Stage Sintering

The equations considered above apply only to the initial stage of sintering in which up to about 5% shrinkage takes place and during which there is very little change in porosity. The intermediate stage of sintering then takes over until the porosity is reduced to between 10 and 5%. After this is the final stage, the pores become isolated from one another and change in shape from cylindrical to spherical. As there is a large change of density during the intermediate stage, it is normal to follow the sintering process by
measurement of the change of a density related property, e.g.
volume shrinkage, porosity, electrical resistivity.

One quantitative analysis of the intermediate stage of sintering
has been made by Coble & Gupta (98) who used porosity to monitor the
sintering process. They assumed that all grains had the same size
and shape and that at any moment during sintering, the pores are
cylinders of the same size residing at three grain edges. If atomic
flux is controlled by diffusion then the flux of atoms from the grain
to the pore surface may be equated to the volume change of the pore.
The isothermal porosity-time data then yield an activation energy
for the densification mechanism. Diffusion coefficients have been
calculated from sintering experiments on alumina and copper powders
and show good agreement with those published by other authors.

Another approach was made by Johnson (113). Making the assumption that
the mechanisms responsible for initial stage sintering also operate
in the intermediate stage he extended his original work. The geometric
substitutions for the flux equations could be taken from microstructures
of the sintered material which are then expressed in terms of the
volume change. The limitation to this method is that surface
diffusion and vapour transport cannot be measured by this method
as they do not affect the geometric parameters. Since these
parameters are determined at the end of a sintering experiment the
results are not affected by any transient phenomena which may occur
during the initial stage of sintering.

As the intermediate stage of sintering is the one in which most
densification occurs it is convenient to relate some function of
length or density to time by an equation of the type:
where $G$ is the density related parameter being measured. This may be linear shrinkage, $\Delta L/L_0$, or volume shrinkage, $\Delta V/V_0$, or the standardised value having a maximum of unity but expressed as, for example:

\[
\frac{L_{\text{initial}} - L_{\text{sintered}}}{L_{\text{initial}} - L_{\text{theoretical}}}
\]

$A$ is a constant and $n$ an exponent which is characteristic of the sintering mechanism, for example, $n = 0.4$ for volume diffusion as in the initial stage. $Q$ is the apparent activation energy, $R$ the gas constant, $T$ the sintering temperature, and $t$ the time of sintering. The value of $Q$ may also be indicative of the sintering mechanism. For example, Johnson & Duwez (114) used this type of equation in a study of the sintering of copper powders and the values of $Q$ they obtained suggest that at temperatures below $1025^\circ C$, surface diffusion was the rate controlling mechanism while volume diffusion was dominant above this temperature. A similar result was found by Reshamwala & Tendolkar (115).

It is possible to use resistivity, $\rho$, as a sintering parameter for conducting materials, as this is related to porosity $\epsilon$, by $\rho = \rho_0 (1-\epsilon)$ where $\rho_0$ is the resistivity of the dense material. A similar equation to the above can be used to deduce an activation energy and an exponent to indicate the sintering process.

This review of sintering theory indicates the measurements to be made in order to determine which sintering mechanisms are operating.
In the following chapter a model is proposed which relates the resistance at the neck between spherical particles and the geometry of the neck. This model will provide a sensitive method for following the sintering process, particularly in the initial stages where measurement of the geometric parameters is difficult.

5.5 Activated Sintering

The presence of an oxide film on powder particles may be said to provide an example of activated sintering. This phenomenon has been examined in the reviews of Moon(101) and of Reshamwala & Tendolkar(120). An extensive study of the influence of thin oxide films on iron, copper, and nickel powders has been carried out by Ramakrishnan & Tendolkar(116). Sintering was carried out in hydrogen or vacuum so much of the oxide is reduced. However, the authors found that sintering could be modified and improved mechanical properties obtained by the presence of an optimum thickness of oxide film and not oxygen content. This thickness was independent of atmosphere, although a reducing atmosphere accelerates sintering due to increased chemical activity. In vacuum and nitrogen accelerated sintering was attributed to increased diffusion in the surface layers, due to defects at the metal-oxide interface. At thicknesses above a critical value gas removal (into vapour in the case of a hydrogen atmosphere) was inhibited so the properties of the sintered compact were adversely affected. The increased sintering time also permitted oxygen solution so that hardness and tensile strength were increased. Oxygen solution was also considered to maintain the defect structure leading to enhanced diffusion and sintering rates indicating the importance of diffusion in the sintering process.
For these three metals, the oxide vapour pressure is high so the evaporation-condensation mechanism of pore rounding could be active at high temperatures. Jordan & Duwez(114) also examined the effect of oxide films on the densification of copper compacts. They suggested that the activation energy for densification could be reduced by using a hydrogen atmosphere to reduce the oxide film which otherwise impeded sintering.

The effect of surface oxide on sintering has also been observed by Solov'eva et al(121). Using a pre-alloyed powder of 80% Nickel - 20% Chromium, they found that an increased oxygen content gave a lower green density and higher sintered density than for unoxidised powder. They suggested that a volatile chromium oxide layer was formed which assisted vapour phase transport.

The importance of volatile oxides has also been stressed by Scott & Butcher(122) and Butcher & Lowe(123) in the sintering of Beryllium powder. The surface layer of oxide inhibited the initial stages of sintering since metal to metal neck formation was retarded. However, in presence of certain impurities, such as silicon, iron, nickel and chromium as found in commercial beryllium, compaction and sintering were observed to be enhanced. It was suggested that the oxide layer was broken by silica which was able to evaporate to form metal to metal necks. Kinetics for such a reaction were favourable.

Thus, some authors believe that oxide films may inhibit sintering in delaying neck formation while others suggest that the increased number of point defects or formation of volatile compounds can reduce the activation energy for sintering.
It was hoped that the resistance method to be described in the following chapter for studying the sintering process would be sufficiently sensitive to determine whether or not oxide films affect the sintering behaviour of titanium powders.

6. A METHOD OF FOLLOWING THE SINTERING PROCESS

In the literature survey, it has been shown that titanium metal always has and oxide film on its surface. For the processing of titanium powders, it is of great interest to be able to account for the behaviour of such films particularly during sintering. Later it will be important to know how quantities of oxygen influence the mechanical properties of the bulk material but the present work is concerned with the behaviour of oxide films in the early stages of sintering.

From the diffusion data, it is seen that an oxide film may dissolve very rapidly at relatively low temperatures but, although the film disappears, it may not reach an equilibrium throughout the particles in the time permitted for sintering. Thus, it is possible that the properties of a powder metallurgical product may not be identical to those of a material which already contains a uniformly dissolved, equivalent quantity of oxygen.

The study of Ramakrishnan & Tendo Ikar(116) on the influence of oxide films on sintering suggests that oxidation may produce an excess of surface vacancies which may help in the activation of the sintering process so that the mechanism of the early stages of sintering may be modified.

Most of the techniques discussed in the previous chapter for sintering studies rely on making measurements of neck diameter at intervals during the sintering process. This requires relatively large powder particles for accurate measurement using metallographic techniques. In the method described here, neck growth information is recorded continuously but not directly and has to be confirmed by metallography.
In order to follow the behaviour of oxide films during sintering, a very sensitive method must be used. Bulk titanium oxide has a very high resistivity and it was shown by Jaffee & Campbell (44) that one atomic per cent of oxygen dissolved in titanium increases its resistivity by about 15% to about 56 µΩcm. Resistivity of titanium dioxide is about $10^{14}$ Ω cm so that the removal of an oxide film will be indicated by a large decrease in the resistance of a compact. Resistivity is also a sensitive parameter with which to observe the growth of necks between particles.

The most common way of following the sintering process using resistance measurement is to express resistivity $\rho$, in terms of porosity $e$, using the relationship:

$$\rho = \rho_o (1 - e)$$

where $\rho$ is the resistivity of the bulk metal. However, this method does not relate to the changes in geometry at the neck between particles. The approach to be considered here is to regard the compact as an array of linear conductors arranged parallel to one another.

Resistance in 3-dimensions has been examined by Maxwell (117) who considered flow of a current through surfaces in the conductor. At the boundary of the conductor there is no current flow, and the conductor is considered to be a tube with current flowing along its axis. Considering sections across the tube, the quantity of electricity entering the tube at one surface must be equal to that leaving at another so the smallest section will limit the current. The conductor may be considered as a cylindrical resistor having this smallest section as its diameter.

If we consider a line of spheres as the resistor then, in simple terms, its resistance, $R$, may be expressed as: 

58...
\[
R_L = \frac{p \ell}{A}
\]

where \(\ell\) is the length of the line of spheres and \(A\) is the area of contact of diameter \(d\). The situation is depicted in the following diagram (figure 8).

**Figure 8: Possible Conduction Path in a Line of Spheres**

The resistor may be considered as a cylinder of diameter \(d\), and, if we consider one sphere, of length \(D\), hence its resistance:

\[
R_s = \frac{4\rho D}{\pi d^2}
\]  
\[\text{(6.1)}\]
If part of the resistance is due to a thickness of oxide film, it may
then be considered as a series resistor made up of the resistance of
metal and the resistance of the oxide.

This formula may be extended to a powder array of lines of spheres,
so that for a compact the total resistance $R_T$ is given by:

$$\frac{1}{R_T} = C \frac{n}{R_L} \quad \ldots \ldots \quad (6.2)$$

The constant $C$ is a geometrical factor; for simple cubic packing $C = 1$. If the compact diameter is $\Delta$ and its relative density $\theta$ then its resistance:

$$R_T = 4 \rho \frac{\pi d^2}{\pi d^2} \cdot \frac{D^2}{\theta \Delta^2} \quad \ldots \ldots \quad (6.3)$$

The model outlined above has the disadvantage in that it only considers the resistance of the central cylindrical portion of each sphere and ignores the contribution to resistance of the bulk of the spheroid material. In the sintering process the neck grows by accretion of material from the spheroid so that the sphere actually decreases in diameter. In the early stages of neck growth for which the equations of Chapter 5 are applicable and which is now considered, this effect may be ignored. The resistance of a sphere-neck pair may be considered as being made up of the resistance of a truncated sphere, and that of a near cylindrical neck made when material from the spherical caps fills the outer portions of the neck creating a region of overlap. The resistance of a line of spheres will be a scale factor times the resistance of one sphere plus one neck. The following diagrams show the neck geometry (figure 9).
Figure 9: Neck Geometry for the Resistance Model

(a) Resistance of truncated spheroid $R_s$:

$$R_s = 2 \int_{0}^{\pi/2} \frac{p}{r^2} \cos \theta d\theta$$

$$= \frac{4p}{\pi D} \left[ \int_{0}^{\pi/2} \log \tan \frac{\theta}{2} \right]$$

$$= \frac{-4p}{\pi D} \log \tan \frac{\theta}{2}$$

... (6.4)
(b) Resistance of Neck, \( R_N \):

\[
R_N = \frac{4pD}{\pi d^2} (1 - \cos \theta_o)
\]

\[
= \frac{4p}{\pi D} \left( \frac{D}{d} \right)^2 (1 - \cos \theta_o) \quad \quad \quad (6.5)
\]

Equation 6.5 above does not allow for the volume of material in the annulus shown in figure 9(c) as ACB and A'C'B', so we shall consider the geometry of this neck in more detail. If it is assumed that the two spheres overlap equally then figure 9(c) shows the geometry where \( \theta_o \) defines the truncated spheroids, and \( \theta_i \) defines the extent of overlap of the two spheres. The infilling volume CAB + C'A'B' may now be compared with the overlap volume CPC' + CQC'.

Overlap volume is given by:

\[
V_o = 2\pi R^3 (2/3 - \cos \theta_i + 1/3 \cos^3 \theta_i)
\]

\[
= \pi R^3 (4/3 - 2 \cos \theta_i + 2/3 \cos^3 \theta_i)
\]

\[
= \pi R^3 \cdot F_1(\theta_i) \quad \quad \quad (6.6)
\]

Infilling volume \( V_1 \) is given by the volume of the cylinder AA'B'B minus twice BOC'B'. The volume of the latter, a truncated spherical cap, is the difference of the two spherical caps, BPB' and CPC'. Thus:

\[
V_1 = \pi R^3 \sin^2 \theta_o (1 - \cos \theta_o) - 2\pi R^3 \left( \cos \theta_i - \cos \theta_o + 1/3 \cos^3 \theta_o \right)
\]

\[
- 1/3 \cos^3 \theta_i)
\]

substituting for \( \sin^2 \theta_o \), and \( \cos \theta_o \) gives:
\[ V_1 = \pi R^3 \left(-\frac{4}{3} + 6 \cos \theta_1 - 8 \cos^2 \theta_1 + \frac{10}{3} \cos^3 \theta_1 \right) \]

\[ = \pi R^3 \cdot F_2 (\theta_1) \]

(6.7)

The relative values of \( F_1 (\theta_1) \) and \( F_2 (\theta_1) \) have been calculated for low values of \( \theta_1 \) (i.e. low values of \( d/D \)) and are compared in the following table:

<table>
<thead>
<tr>
<th>( \theta_1 )</th>
<th>( \theta_0 )</th>
<th>( d/D )</th>
<th>( F_1 (\theta_1) )</th>
<th>( F_2 (\theta_1) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2°</td>
<td>2.83°</td>
<td>0.049</td>
<td>( 8 \times 10^{-7} )</td>
<td>( 8 \times 10^{-7} )</td>
</tr>
<tr>
<td>4°</td>
<td>5.66°</td>
<td>0.099</td>
<td>( 1.18 \times 10^{-5} )</td>
<td>( 1.20 \times 10^{-5} )</td>
</tr>
<tr>
<td>10°</td>
<td>14.16°</td>
<td>0.245</td>
<td>( 4.59 \times 10^{-4} )</td>
<td>( 4.50 \times 10^{-4} )</td>
</tr>
</tbody>
</table>

The values of \( F_1 (\theta_1) \) and \( F_2 (\theta_1) \) are so close as to suggest the identity \( F_1 (\theta_1) = F_2 (\theta_1) \) but re-arrangement shows that:

\[ F_1 (\theta_1) = F_2 (\theta_1) + \frac{8}{3} (1 - \cos \theta_1)^3 \]

It may be concluded, therefore, that the cylindrical volume is almost exactly filled by the overlap material and the value of \( R_N \) in equation 6.5 may be halved to allow for reduced neck length. This only reduces the values of \( R_s + R_N \) by about 10 per cent. The same conclusion may be deduced from the neck volume used to derive the sintering equations as, in the case of overlap, the neck of diameter \( x \) and height \( x^2/a \) yields an expression for resistance:

\[ R_N = \frac{\rho}{\pi a} , \text{ where } a = D/2 \]
This value does not include neck size as a result of the geometric
approximations used. However, the resistance value will be very
low and will have little influence on the total resistance.

Let us consider the case of spheroids of 630 μm having necks ranging
in size from 2% to 60% of the initial diameter. Let the material used
be IMI 130 having resistivity of 48μΩcm. The resistance values for the
two models calculated by equation 6.1 and the corrected equations 6.4
and 6.5 are tabulated below.

Table 10: Resistance calculated using equations 6.4 and 6.5

<table>
<thead>
<tr>
<th>d   (cm)</th>
<th>d/D</th>
<th>θ₀   (degrees)</th>
<th>Rₙ (ohms)</th>
<th>Rₙ + Rₙ (ohms)</th>
<th>Rₙ (ohms)</th>
<th>Rₙ + Rₙ (ohms)</th>
<th>Rₙ (ohms)</th>
<th>Rₙ + Rₙ (ohms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00158</td>
<td>0.025</td>
<td>1.43</td>
<td>0.00425</td>
<td>0.00475</td>
<td>0.00449</td>
<td>1.5521</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00315</td>
<td>0.05</td>
<td>2.63</td>
<td>0.00366</td>
<td>0.00386</td>
<td>0.00390</td>
<td>0.3880</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0063</td>
<td>0.1</td>
<td>5.75</td>
<td>0.00290</td>
<td>0.00314</td>
<td>0.00314</td>
<td>0.0970</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0126</td>
<td>0.2</td>
<td>11.53</td>
<td>0.00220</td>
<td>0.0025</td>
<td>0.00247</td>
<td>0.0240</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0189</td>
<td>0.3</td>
<td>17.47</td>
<td>0.00181</td>
<td>0.00206</td>
<td>0.00206</td>
<td>0.0107</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0252</td>
<td>0.4</td>
<td>23.51</td>
<td>0.00152</td>
<td>0.00177</td>
<td>0.00177</td>
<td>0.0061</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0378</td>
<td>0.6</td>
<td>36.86</td>
<td>0.00106</td>
<td>0.00133</td>
<td>0.00133</td>
<td>0.0027</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is noted that one model predicts a resistance change in the ratio
of nearly 600 : 1, while the other predicts a ratio of 4 : 1 for the
range of neck sizes considered. It is also interesting to note that
the neck resistance, using the corrected form of equation 6.5, is
almost constant. This may be explained simply in that the length increase
of the neck is offset by the increase in neck diameter and the total
resistance decrease is due to the decreased amount of spheroid between
the necks.

It remains to be seen in the following experimental work which model is
applicable and whether such a model may be applied to 3-dimensional
arrays of spheres.
7. EXPERIMENTAL PROCEDURE

7.1 Materials
Starting materials used include iodide grade crystal bar supplied by the Foote Mineral Company, USA, and wrought, commercial purity (IMI 130) bar. The iodide grade crystal bar provided a starting material with very low oxygen content, <200 ppm by weight, and was used for making powder by the hydride-dehydride process described in section 3.4. Hydrogen was then removed by heating in vacuum to leave a metal powder. The wrought, commercial purity bar used for initial experiments was also used for making spherical powders by the centrifugal shot casting process described earlier. The spherical powders were then used in resistance model experiments.

Argon, used as the glove box atmosphere, was evaporated from a tank of liquid argon and circulated by plant, which also contained beds of manganese oxide and calcium for oxygen and nitrogen removal so the gas could be recycled. Purity of the argon was generally better than 20 vpm each of oxygen and moisture for this gas, but could be reduced by a factor of 10 using pure argon which by-passed the circulation plant.

Hydrogen used for the hydriding of metal was purified by use of a palladium diffuser, manufactured by Englehard Industries, and reduced total impurity content to about 1 vpm.

7.2 Powder Characterisation
A variety of powder characterisation methods has been used. Sieving was used to separate the required size fractions of centrifugal shot cast (CSC) powder but, in the case of hydride-dehydride (HDH) powder,
was only used to eliminate the coarse agglomerates (>1 mm), the majority of which were broken by the vibration.

Spheres were separated from the CSC powder by rolling the powder down a gently inclined plane. Only spherical particles would gain sufficient momentum to jump a small gap and roll up another inclined plane, and thus be separated from non-spherical particles. Optical examination was used as an additional check that spheres were selected. These spheres were then washed in acetone to remove any surface contamination prior to use.

Both types of powder were examined by scanning electron microscope (SEM) to observe both the shape and nature of the surface of the powders.

Two additional methods were used to estimate the particle size of the HDH powders; photo-extinction sedimentometry and use of the Fisher Sub-Sieve Sizer.

The photo-extinction sedimentometer measures the intensity of light transmitted by a suspension of the powder in a suitable non-reactive liquid. The logarithm of light intensity is proportional to the concentration of particles of a given size. The maximum size of the sample present at a given time may be calculated using Stokes' equation:

\[ x^2 = \frac{1.8 \eta h}{g + (\sigma - \rho)} \]

where \( x = \) particle diameter (cm),
\( \eta = \) viscosity of the liquid (Pa.s)
\( h = \) sedimentation height (cm)
\( g = \) 981 cm/sec^2
\[ \sigma \text{ is density of sample} \]
\[ \rho \text{ is density of liquid both in g/cm}^3 \]
\[ t \text{ is sedimentation time (sec)} \]

The limitation of this method is that it does not distinguish between single particles and agglomerates. The sedimentation time is related to its density so that for a given time there may be single particles of a certain size and density or agglomerates which act as 'particles' of larger size but lower density.

The results are given as a particle size distribution and the mean particle size may be considered as that size for which the probability of its presence is 0.5.

In the Fisher sub-sieve size, the flow of gas through a bed of powder is measured. The flow rate is a function of pore space, viscosity of the fluid, the length and area of the powder plug, the specific surface of the powder, and the pressure difference across the bed. Hence, if the powder particles are considered to be uniform and spherical, the particle size may be calculated. Again, this method does not distinguish between single particles and agglomerates, and for the above reason gives a result which is weighted towards the finer particle sizes.

Particle size may also be measured by adsorption of layers of gas as in the BET method. However, this method was not used because of the danger of rapid powder oxidation during transfer from the glove box to the BET apparatus. Oxidation experiments were carried out in a glove box atmosphere from which a particle size could be inferred. The oxidation experiments were carried out using a Cahn electro-balance and a chemical balance. Experiments were carried out at room temperature and with the powder heated to 100°C.
using a hot plate while stirring the bed of powder to ensure penetration of the oxygen.

7.3 Pressing

Powder compaction was carried out in a glove box using a 250 KN ring press.

Pellets of HDH powder were made in the form of right cylinders by double ended pressing in a tungsten carbide lined, steel die of 6.35 mm diameter bore. This configuration aimed at achieving uniform density distribution. The die was slightly tapered to facilitate extraction of the pellet and push rods. For each pressing a zinc stearate lubricant was used on the die walls only.

An alumina-lined, brass die was also constructed to enable resistance measurements to be made during pressing.

A Vernier dial was available for measuring displacement of the piston of the press.

7.4 Furnace Design

The sintering furnace (figure 10) consists of a water cooled bell in which there is a molybdenum wire heating element. The furnace is designed to operate at up to 1500°C in a vacuum of 1.33 mPa (10^-5 torr). The hot zone of the furnace is 40 mm long and 40 mm in diameter. The control thermocouple is placed outside the heating coil and a recording thermocouple placed at the bottom of the hot zone. This recording thermocouple is calibrated against thermocouples placed in the specimen position for each of the specimen holders used at all furnace settings and heating rates used. The thermocouples are of the type Platinum + 5% Rhodium - Platinum + 20% Rhodium. The radiation shields are of molybdenum sheet.
Figure 10. The Sintering Furnace.
Power is supplied via a Eurotherm temperature controller, ramp generator and timer, but heating rates are kept low to avoid cracking of the alumina insulating material which acts as former for the heating element.

Fail safe mechanisms are incorporated in the circuit of the control thermocouple so, in case of emergency, if the vacuum or water supply should fail, the furnace would switch itself off.

A vacuum coupling on the top of the furnace is used to insert the specimen holder for dilatometry and resistance measurement.

7.5 Resistance Measurement

Resistance measurement has been carried out using an Automatic AC Double Bridge constructed by Automatic Systems Laboratories Ltd.

This apparatus is capable of measurement of resistances in the range of 1 ohms to 1000 ohms at full accuracy of \( \pm 4 \text{ parts in } 10^7 \) of ratio, or \( \pm 10^{-5} \) ohms in 25 ohms, or in the range \( 10^{-6} \) ohms to \( 10^4 \) ohms at a reduced accuracy of about 4 parts in \( 10^5 \).

The theory of alternating current bridge methods has been discussed in detail by Hague(118). In general, the principle underlying these methods is that the resistance to be measured is incorporated into a network of known conductors similar to the Wheatstone network of direct current theory. Two points of the network are connected to a source of alternating current while another two points are 'bridged' to an instrument which detects alternating current potential differences. The constants of the known conductors are then adjusted so that the two bridged points are at the same potential every instant. This condition may be detected by a zero reading of the detector. Using the known constants of the network
the resistance may be measured. In this case, the resistance of the specimen is compared with a set of standard resistors. The ratio of resistances is varied automatically by servo-motors and the resistance measured when the motor is stationary, indicated by the zero quadrature dial, the current and voltage are in phase and the residual current reduced to zero. This is possible if the frequency of measurement is low so that capacitance between the contacts is minimal. The resistance is derived from a digital display of the resistance ratio where

\[
\text{Resistance Ratio} = \frac{R_{\text{unknown}}}{R_{\text{unknown}} + R_{\text{standard}}}
\]

Precautions taken to reduce error were to use shielded cables between the bridge and the unknown and standard resistances to reduce stray field effects. These cables were also of equal length. Check balances with the leads reversed were made at balance to ensure that capacitance and inductance between the source and bridge were zero. An AC bridge method was chosen in preference to a direct current method to eliminate the possibility of polarisation in oxide films which may have some influence on the sintering behaviour. Also very little power (less than 0.1 watts) is dissipated in the resistance elements which include the material being sintered. Connection of potential and current leads to the specimen was made in the case of compressed pellets by pressing a platinum foil to the ends of the pellet. Platinum wires were also used inside the furnace. At high temperatures, i.e. greater than 1,000°C, titanium wires and foils were used as, above this temperature, diffusion of platinum into titanium was appreciable forming intermetallic compounds of high resistance. At low temperatures, it was
advantageous to use platinum wire and foil for the contacts as these could be welded together conveniently ensuring good electrical contact. In the case of single lines of spheres, contact was made simply by pressing the wire onto the spheres at the ends of the line.

The contact wires were sheathed in alumina and incorporated in the specimen holder.

7.6 The Dilatometer

The dilatometer was constructed using equipment manufactured by Vibro-Meter AG. Length changes were detected using an inductive displacement transducer, type MS/1275, having a sensitivity of 0.03 mV/V/μm. This was powered by and the output signal amplified by a Carrier Frequency Amplifier, type 8MC-1/A AO, which also provided an input to a chart recorder. The maximum operating temperature of the transducer is 70°C, and it therefore has to be kept isolated from the specimen using a push rod in the specimen holder, while keeping the transducer in a cool part of the vacuum chamber eliminating the need for excessive vacuum seal. Insulated electrical contacts were made through the wall of the vacuum chamber. The specimen holder and push rod were machined from annealed molybdenum bar and the specimen holder was insulated to prevent the short circuit of resistance contacts on its walls. The transducer is fixed relative to the specimen holder so only the push rod is free to move. The dilatometer is shown schematically in figure 10(a).

Calibration was carried out using a machined standard of fully dense titanium.
Figure 10a. Schematic diagram of the dilatometer.
7.7 Examination of Specimens

The density of as-pressed pellets was measured in glove box atmosphere by weighing the specimen on a chemical balance and measuring its dimensions using a micrometer.

The density of sintered pellets could be carried out in the same way but also could be measured by xylene displacement using the following procedure:

1. The pellet is weighed in air, \( W_1 \).
2. A wire is tied to the pellet which is then immersed in xylene and placed in a vacuum dessicator to displace air trapped in open porosity or pressing faults.
3. The pellet in the xylene was removed from the dessicator and the pellet suspended by its wire from the balance beam while immersed in the xylene to give \( W_2 \).
4. The pellet was removed from the xylene and excess liquid removed from its surface. The pellet and wire were then re-weighed, \( W_3 \), while suspended above the beaker of xylene, i.e. in air saturated with xylene vapours.
5. The pellet was removed from the wire and the wire re-weighed in xylene vapour, \( W_4 \).
6. The wire was immersed in the xylene to the same depth as when it carried the pellet and was then re-weighed, \( W_5 \).
7. The specific gravity (SG) of the xylene was measured.

The bulk mean density is then given by:

\[
BMD = \frac{W_1 \times SG}{(W_3-W_4) - (W_2-W_5)}
\]

Repeated measurements on the same specimen show that values are reproducible to within 1.5%. The theoretical value for the density of titanium was taken to be 4.51 gm/cm\(^3\).
Metallography

Some specimens were examined under the optical microscope. They were mounted, ground on silicon carbide paper down to 600 grit, followed by polishing on the 3 μm diamond compound wheel. The final stage of polishing was carried out using a suspension of gamma-alumina in distilled water. Certain specimens were etched using Kroll's reagent which consists of 96 parts distilled water, 2 parts nitric acid, and 2 parts hydrofluoric acid. The specimen was swabbed with this solution, rinsed with water and then with sodium bicarbonate solution to neutralise the hydrofluoric acid before a final rinse and drying.

Scanning electron microscopy was used to examine the necks between particles obtained on sintering single lines of spheres. Pairs of spheres were mounted on the microscope stub end on, so that in some cases both surfaces of the neck fracture could be observed.

8. RESULTS AND DISCUSSION

8.1 Powder Manufacture

The hydride-dehydride (HDH) process was chosen as a suitable route using high purity titanium bar prepared by the iodide process and hydrogen of better than 1 ppm oxygen. The hydriding conditions were chosen to produce a powder of mean particle size in the range of 1-10 μm. Such a particle size would ensure sufficient oxide to produce a detectable influence of oxide films on the sintering behaviour.

Hydrogen has a very low solubility in α-titanium, its maximum solubility being 7.9 atomic percent at about 300°C, so that hydride formation is possible at low temperatures. The compound TiH₂, readily formed in
the presence of hydrogen, is very brittle and may easily be milled to form a fine powder. For convenience, it is desirable to heat the titanium or reduce its bulk to speed the kinetics of formation of titanium hydride. The phase diagram of figure 5 shows the hydride cannot be formed above about 600°C, and only a β-phase solid solution will exist. This cannot easily be broken to a fine particle size. At temperatures up to 500°C the hydride will readily form under hydrogen at atmospheric pressure. Hydriding was carried out by heating about 30 g of 12.5 mm diameter crystal bar in a stream of pure hydrogen at atmospheric pressure and a flow rate of 5 cm³/min. The phase diagrams show the lowest temperature for hydride formation to be 320°C, but at this temperature attainment of equilibrium was too slow to be carried out in an overnight cycle. At 450°C the β-solid solution is rapidly formed and, on cooling this decomposes to form the γ-solid solution whose composition approximates to that of the brittle hydride. Hydriding was therefore carried out by heating titanium at temperatures between 320°C and 500°C for 2 hours and cooling in hydrogen. The hydride was then milled in a vibratory mill by attrition between tungsten carbide balls in a tungsten carbide lined mill pot. Milling was carried out for various times and the product examined using a scanning electron microscope. After 4 hours milling (figure 11), the powder consisted of small agglomerates (about 10 μm diameter) of fine powder. After 8 hours (figure 12) larger balls of up to 200 μm diameter were observed and these agglomerates were more numerous after 12 and 16 hours of milling. This is a result of the tumbling action of the mill, and indicates that no advantage is to be gained...
11, 12 Titanium Hydride after 4 and 8 hours milling respectively

13 Powder hydrided at 500°C, milled for 4 hours and dehydrided at 600°C
by milling for longer than 4 hours. There was no apparent difference in milled particle sizes of powder hydrided at 400°C and 500°C, and the upper temperature was chosen for subsequent hydriding to enable the reaction to be carried out quickly. It was noted earlier that Hohmann(17) selected 450°C as the optimum hydriding temperature after initial heating at 600°C to clean the surface of the titanium of oxide and magnesium, and thus speed the diffusion of hydrogen to the interior of the sample. The starting material used by Hohmann was alloyed titanium or titanium scrap, which are both reported to be more difficult to hydride than pure titanium and hence the high initial temperature.

The conditions for dehydriding are chosen with the aid of the pressure-concentration isotherms derived by McQuillan(27), figure 6. These curves indicate the pressure and temperature to be used to produce material of known hydrogen content. For example, at 600°C and pressure of 1.33 mPa (10^-5 torr) a hydrogen concentration of 10 ppm may be achieved. Gavrilova(75) stated that 600°C should be the maximum temperature for dehydriding unless an anti-sintering agent, such as calcium oxide, is present. This would allow dehydriding to be carried out at up to 900°C with increased effectiveness at a given pressure but then presents the difficulty of its removal. In this work, no such additions were used. 30 g samples of hydride powder were slowly evacuated in the dehydriding furnace to 1.33 mPa and then heated to the chosen temperature until hydrogen ceased to be given off, i.e. until the vacuum had returned to its initial value. The powders were then examined by scanning electron microscopy.
Powder hydrided at 500°C, milled for 4 hours, dehydrided at 500°C

Powder hydrided at 500°C, dehydrided at 600°C, milled for half an hour and 2 hours respectively
Powder dehydrided at 600°C (figure 13) had many coarse agglomerates of powder which had become partially sintered. These agglomerates were quite friable but some particles of up to 1 mm diameter still remained after sieving.

Powder dehydrided at 500°C (figure 14) was yet more friable as sintering had taken place to a lesser extent. The largest agglomerates observed in this case were 200 μm across but many were less than 50 μm. Closer examination of these particles revealed the presence of a rough surface composed of particles many of which were less than 4 μm in diameter. These particles appeared to have rougher surfaces than those dehydrided at 600°C.

In order to break up these agglomerates, some powder which had been dehydrided at 600°C was ball milled as in the previous manner and samples removed at intervals for examination in the scanning electron microscope. Rather than breaking the agglomerates, they became welded together after as little as 30 minutes (figure 15). These agglomerates became more consolidated and increased in size with further milling (figure 16).

Material dehydrided at 500°C showed a similar initial behaviour (figure 17) with agglomeration of fine particles, but after 40 minutes flattened agglomerates were observed which were breaking up into platelets of about 100 μm across (figure 18). This powder still contained sufficient hydrogen to make it more brittle than that dehydrided at 600°C. The residual hydrogen could also activate the sintering process. This was confirmed when a pellet made from this material gave off hydrogen during sintering and reached 98% theoretical density, whereas powder dehydrided at the higher temperature and containing hydrogen sintered to between 90 and 94%.../
17. Powder hydrided and dehydrided at 500°C, milled for 30 and 40 minutes respectively.

18. Powder hydrided at 500°C, milled for 4 hours, 2-stage dehydriding at 400 and 600°C.
density under the same conditions. These results suggest that most of the hydrogen should be removed at as low a temperature as possible to prevent sintering, and then the powder heated to $600^\circ C$ to reduce the hydrogen content to about 10 ppm in a vacuum of 1.33 mPa.

Dehydrdriding was therefore carried out by heating in vacuum at $400^\circ C$ to remove the majority of gas. At this temperature and 1.33 mPa, only 100 ppm of hydrogen remained. The powder was still in its finely divided state and a final heating to $600^\circ C$ at $10^\circ C/\text{minute}$ removes the remaining hydrogen to a concentration of 10 ppm. Agglomerates of the very fine powder are shown in figure 19. The surface roughness of this material appears greater than that obtained in the previous treatments. The time required for a 30 g batch of powder to be dehydrdred was about 16 hours at $400^\circ C$ and 1 hour at $600^\circ C$, but temperature and pressure conditions in the furnace determined the end of the process.

The HDH process was carried out on a sample of Ti-6Al-4V made by arc melting. The powder obtained was similar in size and appearance to the elemental powder. It was suggested by Pittinato & Hanna(119) that the interstitial hydrogen tends to be concentrated in the $\beta$-phase causing its lattice to expand. The surrounding $\alpha$-phase deforms elastically with the resultant stresses assisting the cracking of the alloy and penetration of hydrogen. Thus, it seems likely that the HDH process would be very successful in making alloy powder.

An experiment on wrought commercial purity (IMI 130) bar, required longer time for hydriding than did the iodide crystal bar. This is probably due to the porosity of the latter facilitating hydrogen penetration.
The scanning electron microscope study above shows that the HDH route can be used to make powder from iodide purity titanium. The powder is prepared by heating the titanium in flowing hydrogen at 500°C followed by ball milling for 4 hours. The metal powder is then produced by a 2 stage dehydriding process in vacuum (1.33 mPa) at 400°C and 600°C, thus avoiding sintering of the powder. The metal powder consists of agglomerates of particles of about 20 μm across, but containing finer particles of about 4 μm diameter giving the particles rough surfaces and high porosity (figure 19).

Spherical particles for use in the sintering model experiments were manufactured at AERE, Harwell, by the centrifugal shot casting process described in Chapter 3. As a range of particle sizes and shapes is produced, these first have to be sorted. The appropriate size fractions, 125 to 180 μm for the packing experiments, and 600 to 650 μm for the sintering model experiments. Spherical particles were then selected by rolling particles down a plane inclined at approximately 20° to the horizontal. Spherical particles would gain sufficient speed to jump a gap into the collecting container. For the model experiments individual spheres were then optically selected.

8.2 Oxidation

As indicated in an earlier section, the oxidation behaviour of metal powders is considered to be no different from that of bulk metal with one major exception, which concerns the dissipation of the heat of formation of the oxide layer. For powders the rate of heat removal is limited by restricted conduction paths between particles and a significant rise in temperature will increase the rate of oxidation and cause a fire.
Figure 20. Room temperature oxidation of Titanium powder in box atmosphere of Argon +20ppm Oxygen.
The oxidation of some samples of freshly made HDH powder was studied by continuous weighing in a glove box atmosphere of argon containing about 20 ypm oxygen, i.e. $Po_2 = 2.0 \text{ mPa (1.5 } \times 10^{-2} \text{ torr)}$. The weight gain is plotted in figure 20. Oxidation initially obeys a logarithmic law in agreement with the behaviour observed by other authors. The reaction stops after about 2 days when a stable oxide film is formed. The weight gain in this case was 0.11%. If it is assumed that the stable oxide film formed at room temperature is 4.5 nm as found by Andreava(63) then, using the nomographs of Russell(3), a mean particle size of 7.0 $\mu m$ is indicated. This assumes a uniform oxide layer is formed over a spherical surface. Oxygen analysis of this material by the vacuum fusion method gave an oxygen content of 0.13 wt%. This suggested that the oxygen content of the iodide starting material was about 200 ppm and this was confirmed by analysis. These results suggest that little contamination takes place during the hydride-dehydride route for powder production.

Another sample of powder was heated to constant weight at 100°C in the same atmosphere and an increase in weight of 0.16% was recorded. At temperatures above ambient, a thicker oxide film is formed and, using Russell’s nomograph for this size of particle, 7.0 $\mu m$, and this weight increase, an oxide film thickness of 20 nm is suggested. This result is reinforced by the work of Smith(98) who measured a limiting film thickness of 16 nm using ellipsometry on bulk material, which had been oxidised at temperatures between 24°C and 250°C in an oxygen pressure of 2.66 mPa (2 $\times 10^{-5}$ torr).

The oxidised powder from the above experiments was retained for subsequent experiments to examine the effect of oxidation on the pressing and sintering behaviour of powders. A difference in
behaviour may be expected as there is a large difference in oxide film thickness but little increase in particle diameter.

8.3 Particle Size Measurement

As has already been mentioned, SEM examination of HDH powder shows rough, equi-axed particles mostly of about 4 μm in diameter present in agglomerates of about 20 μm diameter. The appearance and size of this powder was little different from that of the titanium hydride from which it is made except that the hydride appears to have a rougher surface. It was noted that if dehydrating is carried out by heating directly to 600°C, the metal powder obtained is partially sintered but that if the 2 stage process was used a friable powder was obtained. As this process was to be used for powder production, it was necessary to find out whether sintering occurred so particle size measurement was carried out on both the hydride powder and HDH powder by use of the Fisher sub-sieve sizer and the photo-extinction sedimentometer. All samples were taken from one batch of hydride material from which all samples of HDH powder were made in one batch. Hence, the number of samples is limited but comparison of results may be made safely. The results are presented in table II.

Table II: Particle Size (microns)

<table>
<thead>
<tr>
<th></th>
<th>Fisher</th>
<th>Sedimentometer</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiH₂</td>
<td>3.1, 3.3, 3.2</td>
<td>6.6, 13.0, 14.3, 7.8, 10.4 ± 3.8</td>
</tr>
<tr>
<td>HDH</td>
<td>9.3, 5.7, 7.5</td>
<td>8.0, 17.0, 14.0, 10.9, 12.5 ± 3.9</td>
</tr>
</tbody>
</table>

Only 2 samples of each powder were measured by the Fisher method and the arithmetic mean is given. The sedimentometer uses less
material and 4 results with their mean and standard deviation are given. The suspending medium for the powder was chloroform. The most noticeable difference in these results is that the Fisher method indicates a much finer particles size than the sedimentometer. However, the sedimentometer does not differentiate between single particles and agglomerates which behave as large particles. The sedimentometer results show only a slight increase in particle size on dehydriding, from 10.4 to 12.5 μm, but these results lie within one standard deviation. Therefore, it must be concluded that little sintering takes place in the 2 stage dehydriding process used. The Fisher results suggest that particle size increases from 3.2 μm to 7.5 μm on dehydriding. However, the effect of heating of the hydride powder may cause a reduction in the surface roughness of the particles. This in turn causes a reduction in surface area, which is the parameter measured by this method from which particle size was deduced. The reduction of surface area then implies a larger particle size.

The oxidation experiment also suggests a particle size of 7.0 μm for the HDH powder so this figure was used for the resistance experiments.

8.4 Pressing

Pellets of about 0.5 g weight were made from several powders and pressed at different pressures. Three batches of powder were used:
(a) Powder exposed to glove box atmosphere at room temperature;
(b) Powder exposed to the same atmosphere at 100°C;
(c) Powder made by dehydriding at 500°C, in place of the 2 stage process finishing at 600°C, and then exposed to glove box atmosphere.
Figure 21. Variation of pellet resistance during pressing.
The nature of oxide film has been indicated in experiments in which the resistance changes of a pellet of oxidised powder have been followed using the AC bridge during pressing, using the method described in Chapter 7.5. The variation of resistance of a sample of 0.5 g of freshly prepared HDH powder is shown in figure 21.

After an initial curved portion, the logarithm of resistance versus pressure curve becomes linear. As indicated in Section 4.2 dealing with theoretical aspects of consolidation, this is the stage when plastic deformation of powder particles is taking place. The initial curvature is due to particle reorientation and slip into more favourable positions. The experimental points show a close fit to a smooth curve and the resistance values suggest that only a small amount of oxide film is present. Should a continuous oxide film of 5 nm be on the surface of particles of diameter 7 µm, then using equation 6.3 a resistance of several milli-ohms would be recorded.

It may be that the sliding of particles over one another and the pressing action has broken the oxide film to give good metal-to-metal contact. This may have also contributed to the initial section of the curve.

A series of pellets was pressed at each pressure between about 463 mPa (30 ts) below which the green strength was very low, and 1235 mPa (80 ts). The results are plotted as log density versus pressure in figure 22.

As expected the results show a linear variation of log density with pressing pressure between about 65 and 80% of theoretical density for each type of powder. Of the 2 HDH powders in which the final dehydrating stage takes place at 600°C, the oxidised powder, b,
Figure 22. Variation of Density with Pressing Pressure.
HDH powder, 4/600°C treatment, exposed to box atmosphere at 20°C, x; 100°C, ○;
HDH 500°C treatment, exposed to box atmosphere at 20°C, □.
compacts to a lower density for a given pressure than the
unoxidised powder, a. This contradicts the work of Machlin(86)
who found a lubricating effect due to the oxide film which should
assist compaction. It is possible that the oxidation process has
caus ed a slight roughening of the particle surface so that it will
not pack to such a great density as the unoxidised powder, but
SEM examination of the powder could neither confirm nor reject this
assumption.
The powder dehydrided at 500°C (c) packs to an even lower density
and this is most certainly due to its greater agglomerate size, as
shown by scanning electron microscopy. Powder dehydrided at 600°C
(a), figure 13, shows a much smoother surface than that dehydrided
at 500°C (c).
For the sintering experiments, a compaction pressure of 617 MPa
(40 tsi) has been used throughout as this was found to give sufficient
green strength and reproducible density. The foil contacts used for
resistance samples were also firmly fixed using this pressure.

Packing of Spheres

The packing of spheres was also examined as this was important for
application of the resistance model to 3-dimensional arrays of spheres.
The spheres were packed in a cylindrical pot cut from alumina tube
having the same dimensions as a pellet, i.e. its internal diameter
was 5 mm. Different size fractions of spheres were packed in order
to choose the size of sphere which most closely resembled the
closest random packing density, 64%, achieved by Bernal(79). Of
the size fractions examined, spheres in the range 125 - 180 μm diameter
most closely reproduced the above density as, in the size of
container used for sintering such compacts, larger sized spheres
would form regular packed arrays at the sides of the container and
reduce the density. It was hoped that this structure would provide
an intermediate stage between the resistance model and the random
array of the HDH metal powder.

8.5 Sintering of Compacts

Initial sintering experiments were carried out under a variety of
conditions. The hydride powder has been sintered to 97% theoretical
density after 1 hour at 1350°C in vacuum. Metal powder prepared by
the HDH route from commercial titanium (IMI 130) pressed at 617 mPa
(40 tsi) and in the same conditions sintered to about 80% of full
density. Metal powder prepared from pure titanium by the HDH route
sintered to a slightly greater density (90%) under the same conditions
suggesting that impurities present in commercial titanium inhibit
the sintering process. A similar result was found by Goetzel &
de Marchi(16), who compared the spark sintering of magnesium reduced
sponge and the purer, sodium reduced sponge. The latter sintered
to a slightly greater density than the magnesium reduced sponge.
Specimens which were sintered using platinum foil contacts for
resistance measurement experiments, were heated at 13°C/min to a
sintering temperature of approximately 1250°C and held at this
temperature to observe sintering. At higher temperatures, an
eutectic of titanium and 40% by weight of platinum is formed which
melts at 1310°C. Sintering under these conditions enables a density
of about 93% to be obtained after 2 hours at the sintering
temperature. In addition to resistance measurement the sintering
process was followed using a recording dilatometer. A typical set of
curves obtained in 2 sintering cycles is shown in figure 23.
Figure 23. Typical sintering curve.
During the sintering cycle, the increase in temperature causes an initial increase in length and resistance, but later there is competition between sintering and oxide solution processes. At temperatures between 500°C and 600°C, there is a contraction which may be associated with the solution of oxide film which is very rapid at this temperature. Calculation shows this shrinkage to be about that expected in a 5 mm long compact from complete solution of a 5 μm film on spherical particles of 7 μm diameter, but the absolute value of this shrinkage is obscured by such processes as particle re-orientation. On a second heating cycle under the same conditions, i.e. heating at 13°C/minute to 1250°C in a vacuum of 6.65 mPa (5 x 10⁻⁵ torr), a contraction at this temperature was not observed. This confirms that oxide solution or particle re-orientation was responsible for the shrinkage observed at 500-600°C in the first sintering cycle but does not distinguish between the 2 processes, although such a rapid change is more likely to be explained by the former process.

A second contraction and reduction in resistance was observed at about 880°C denoting the α to β phase transformation. As the temperature was further increased, the resistance of the compact increased until at about 1000°C a steep drop in resistance, but without dilation, suggests neck growth is taking place without shrinkage. This indicates neck growth by surface or volume diffusion from the surface or vapour transport. At the sintering temperature, a slow decrease in both resistance and length was recorded. These changes are not as large during the second cycle. The resistance data obtained from the isothermal sintering stages did not enable sintering rate exponents to be deduced.
Application of equation 6.3:

\[
R_T = \frac{4\rho \lambda}{\pi d^2} \frac{D^2}{8A^2}
\]

to experimental data gave a value of resistivity of the correct magnitude. For example, HDH powder in a pellet of length and diameter of 5.0 mm sintered to 93% density and a room temperature resistance of about 0.01 ohms. Assuming the particle size to be 7.0 \( \mu \text{m} \) and \( d/D \) from micrographs of spheres sintered under the same conditions to be 0.1, then resistivity is about 50 \( \mu \text{cm} \) compared with a reported value of 42 \( \mu \text{cm} \) for pure titanium. This level of resistivity may be expected from figure 2 to be that associated from the solution of 1 atomic percent (about 3000 ppm by weight) of oxygen, but this value is higher than that shown by analysis (about 1200 ppm).

Apart from oxide solution, it was assumed above, that a reduction in resistance could be accounted for by particle re-orientation to give a more dense structure. However, an experiment using centrifugally shot cast (CSC) spheres shows this to be untrue. Spheres of a narrow size fraction were packed into a small alumina pot layer by layer to give as high a packing density as possible. The specimen was then heated to 1250°C and sintered for a short time to allow necks to form between particles. The micrograph of a section at the axis of the specimen (figure 24) shows areas of intense local sintering, as well as areas where little or no sintering has taken place, and large areas of porosity. The apparent density before and after sintering were both about 64% and shrinkage about \( 1\frac{1}{2} \% \). The areas of high porosity may therefore account for an increase in resistance.
24. Section through compact of spheres. 15X

25. Extent of diffusion of platinum contact into sphere. 120X
8.6 Sintering of Lines of Spheres

8.6.1. Resistance Measurement

From the above experiments on compacts of hydride-dehydride and spherical powders, it can only concluded that quantitative analysis of the sintering process by resistance measurement is very complex. A simpler sintering model using a single line of spheres would be advantageous before extending it to 3-dimensional particle arrays. Analysis of results from sintering of compacts in terms of the resistance model is very complex so, in order to examine equations 6.1, 6.4 and 6.5 in more detail, single lines of spheres were sintered. Only resistance measurement and metallography have been used to examine the sintering behaviour. The sintering experiments were carried out by placing the required number of spheres in a narrow bore alumina tube using platinum or titanium wire contacts to follow resistance changes. Platinum wires were used at low temperatures where the extent of reaction with titanium was small. The extent of this reaction at 1030°C is indicated by the micrograph in figure 25, and a comparison of the resistance results shown in table 13. The normalised resistance values for experiments using platinum contact wires (PW 126) and titanium contact wires (PW 133) are very close, 0.0079 ohms and 0.0077 ohms respectively, showing that this level of interaction has little influence on results. The extent of reaction is greater at higher temperatures for which reason only titanium wire contacts are used.

For these experiments, spheres in the size range 600-650 μm were selected and measurement of the lengths of the lines suggested that the mean value of diameter was 630 μm. In the first experiments, a column of spheres was heated to 625°C repeatedly to remove any
adsorbed gas layer as indicated by a stable room temperature resistance value. The heating rate used was \(10^\circ C\) per minute and the time at temperature was 1 hour. The experiment was repeated using the same heating rate but holding at \(1030^\circ C\) for 1 hour and cooling between runs to measure room temperature resistance. The experiment was repeated using columns of different numbers of spheres and the results presented in Table 12. Included in the table is the final value of resistance per sphere.

Table 12: Desorption of Gas as shown by Room Temperature Resistance Values

<table>
<thead>
<tr>
<th>Heating Cycle</th>
<th>Maximum Temp. (^\circ C)</th>
<th>Holding Time (hrs)</th>
<th>Resistance (ohms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>625</td>
<td>1</td>
<td>PW 123 52 Spheres</td>
</tr>
<tr>
<td>2</td>
<td>625</td>
<td>1</td>
<td>PW 124 34 Spheres</td>
</tr>
<tr>
<td>3</td>
<td>625</td>
<td>1</td>
<td>PW 125 9 Spheres</td>
</tr>
<tr>
<td>4</td>
<td>1030</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1030</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1030</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Resistance/Sphere</td>
<td></td>
<td></td>
<td>PW 123 52 Spheres</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>PW 124 34 Spheres</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>PW 125 9 Spheres</td>
</tr>
</tbody>
</table>

The first part of the experiment, the heat treatment stage at \(625^\circ C\) is completed after 2 hours. This stage allows gas desorption and oxygen solution to take place and was seen to be complete by the very small reduction in resistance after the third hour at temperature. Thus, in all subsequent experiments using CSC spheres, a heat treatment of 2 hours at \(625^\circ C\) was used. The second part of the experiment at the higher temperature, is the sintering cycle and in subsequent experiments, this was carried out continuously for
3 hours. The results in table 12 also show a value for resistance per sphere which is almost the same for the 3 columns of spheres. This suggests that the contact error at the ends of the line (a platinum-titanium contact in this case) is small and agrees with the earlier conclusion that at this temperature the reaction between titanium and platinum has little effect on resistivity. A further comparison was made at 1240°C where the resistance/sphere using platinum wires (PW 129) was 0.0100 ohms while the corresponding value using titanium wires (PW 135) was 0.0028 ohms. The material near the wire contacts in the first of these experiments was very brittle and this was attributed mainly to interaction between titanium and platinum to form an intermetallic compound. This error could be eliminated if contact could be made on the specimen after it had been removed from its tube but, in practice, this proved difficult to carry out. Further sintering experiments were carried out at 1424°C using titanium contacts (PW 134) and at 625°C (PW 127), and 825°C using platinum contacts. The heating curves for the sintering treatments of these lines of spheres are shown in figure 26. These curves show a similar heating behaviour. The absolute resistance values differ as a result of the different numbers of spheres in each line. The gradient of these curves decreases at about 600°C, due partly to further gas desorption but mainly to the onset of sintering. Scanning electron microscope examination of the specimens after sintering showed distinct necks were formed at 825°C (PW 128), but there was no evidence of neck growth below this temperature. The α→β transformation was shown by a large decrease in resistance at about 880°C. The high temperature experiment showed an increasing resistance as the sintering temperature of 1424°C
Figure 26. Heating curves for single lines of spheres.
Figure 27. Comparison of oxidised (133) and unoxidised (126) spheres.
was approached, and this was attributed to a reaction with the alumina tube. Hohmann(17) reported that alumina is only partially stable against titanium in high vacuum. Some solution is evident at 1200°C and strong solution of alumina occurs at 1400°C causing embrittlement of the titanium. On removal from the furnace, this specimen was very brittle and only a few neck measurements could be made.

A comparison of the heating curves of strongly oxidised (PW 133) and unoxidised (PW 126) samples has also been made in figure 27. Spheres were oxidised by heating slowly in air to a uniform colour. The oxidised spheres had a yellow oxide layer which from Flower's work (69) corresponds to a thickness of 40 nm. Both experiments used the same number of spheres, 32, and were sintered at 1000°C after the normal heat treatment. The oxide film alone accounts for the resistance difference in this case. It may be seen that the resistance of the oxidised spheres decreases sharply at about 500°C as rapid solution of the oxide film takes place. At 650°C oxide solution is complete and the 2 curves become very nearly super-imposed. This layer of oxide corresponds to an increase of 0.02 wt% oxygen when it is fully dissolved in a 630 μm sphere and will therefore not affect resistivity of the bulk material to any great extent. The resistivity would possibly be increased from 48μΩ·cm for this material to about 50μΩ·cm as it requires 1 wt% oxygen to increase resistivity of iodide titanium from 47μΩ·cm to 56.6μΩ·cm, as indicated in figure 2 from the work of Jaffee & Campbell(44).

The results of these sintering experiments are tabulated in table 13 showing the sintering temperature, the resistance measured at room temperature after sintering, R, the number of spheres, N, and the resistance per sphere, R/N.
Table 13

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Sintering Temperature °C</th>
<th>N</th>
<th>R (ohms)</th>
<th>R/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>PW 126</td>
<td>1030 Pt contacts</td>
<td>32</td>
<td>0.2476</td>
<td>0.0077</td>
</tr>
<tr>
<td>PW 127</td>
<td>625 &quot; &quot;</td>
<td>25</td>
<td>0.4174</td>
<td>0.0167</td>
</tr>
<tr>
<td>PW 128</td>
<td>825 &quot; &quot;</td>
<td>34</td>
<td>0.4345</td>
<td>0.0128</td>
</tr>
<tr>
<td>PW 129</td>
<td>1240 &quot; &quot;</td>
<td>52</td>
<td>0.3234</td>
<td>0.0100</td>
</tr>
<tr>
<td>PW 133</td>
<td>1030 Ti contacts</td>
<td>38</td>
<td>0.2833</td>
<td>0.0074</td>
</tr>
<tr>
<td>PW 134</td>
<td>1424 &quot; &quot;</td>
<td>32</td>
<td>0.10379</td>
<td>0.00325</td>
</tr>
<tr>
<td>PW 135</td>
<td>1240 &quot; &quot;</td>
<td>33</td>
<td>0.09201</td>
<td>0.00279</td>
</tr>
</tbody>
</table>

8.6.3. Specimen Examination
The sintered lines of spheres were broken from the alumina sheath for neck measurement. This was first attempted by successive sectioning of the specimen perpendicular to the neck. However, this was not totally reliable as, in many cases, there spheres were not perfectly round and the diameter measured at the widest neck section would not then reflect the true contact area. These sections were of great value to examine the penetration of platinum (figure 25) for examining the linearity of the columns of spheres (figure 28), and for carrying out hardness measurements which reflected the oxygen content of the material. The necks were first examined using scanning electron microscopy before sectioning.

Pairs of spheres were broken from the line of spheres and mounted end upwards in colloidal graphite on the metal SEM stubs. In some cases the spheres were mounted so that both sides of the neck fracture could be observed. Micrographs of the necks were taken so that measurement of the neck area could be made by tracing round the neck on tracing graph paper. This area was then used to calculate the equivalent circular diameter (ECD) of the neck. As many neck measurements as
28. Alignment of column of spheres. 30X

29. As-received centrifugally shot cast particle

30. Detail of sphere surface after sintering at 1030°C. 2000X
31, 32, 33 Necks on spheres sintered at 1040°C. Equivalent circular diameters of 70, 58 and 73 μm
34, 35, 36 Necks on spheres sintered at 1040°C. Equivalent circular diameters of 72 and 88 μm. 35 and 36 are two fracture surfaces of one neck. 1000X
37, 38, 39 Necks on spheres sintered at 1040°C. Equivalent circular diameters of 57, 60, 73 microns. 1000X
40, 41, 42 Necks on spheres sintered at 625°C. Equivalent circular diameters 45, 59 and 38 microns
43, 44, 45 Necks on spheres sintered at 825°C. Equivalent circular diameters of 39, 37, 31 μm
46, 47, 48 Necks on spheres sintered at 825°C. Equivalent circular diameters of 23, 19, 39 μm
49, 50, 51  Necks on spheres sintered at 1240°C.
Necks on spheres sintered at 1240°C. Equivalent circular diameters of 77, 129, 127 µm. 480X
55, 56, 57 Necks on spheres sintered at 1240°C. Equivalent circular diameters of 104, 111, 141 μm. 480X
Necks on spheres sintered at 1040°C. Equivalent circular diameters of 80, 84, 71 µm
61, 62, 63 Necks on spheres sintered at 1040°C. Equivalent circular diameter of 72, 65, 76 μm
64, 65, 66 Necks on spheres sintered at 1040°C. Equivalent circular diameter of 74, 63, 76 μm
67, 68, 69 Necks on spheres sintered at 1040°C. Equivalent circular diameter of 73, 79, 78 µm
Neck on sphere sintered at 1040°C. Equivalent circular diameter 74 μm

Small sphere adhered to surface of large sphere before heating and after recrystallising at the sintering temperature of 1040°C
73, 74, 75 Neck of spheres sintered at 1424°C. Equivalent circular diameter of 201, 143, 213 μm
76, 77 Neck on spheres sintered at 1424°C. Equivalent circular diameters 216, 253 μm

79 Hardness traverse of sphere heated at 1424°C
possible were made but no necks were observed for the low temperature specimen (PW 127) sintered at 625°C.

The as-received spheres of commercial purity titanium (figure 29) have a slightly roughened surface, probably as a result of the start of dendrite formation during cooling. Many of the sintered spheres, especially those sintered at high temperature, had a step-like structure on the surface (figure 30). This was also observed on separate spheres heated at high temperature and could be due to recrystallisation resulting from the stresses created during the solidification stage of the centrifugal shot casting process. Neck regions appeared to be free of this structure. Scanning electron micrographs of necks are shown in figures 31 to 77. Except for the specimen sintered at 1424°C (figures 73-77), the necks generally show a ductile type of fracture, and there was no evidence of oxide or other inclusions which would have been shown by charging of the specimen in the electron beam. The neck areas were not always circular as few of the original particles were perfectly spherical. Some of the necks appeared to have areas within them where contact between particles had not taken place (e.g. figures 31, 41, 52, 56 and 69) or had more than one main area of contact (e.g. figures 39, 52, 56). The total contact area was measured from the micrographs so that calculation of an effective neck diameter was possible. The results with mean values and standard deviation, $\sigma$, are presented in table 14, with values of $d/D$ where $D = 630$ microns.

The table shows the increase in neck size with increasing sintering temperature. The neck sizes of oxidised spheres sintered at 1040°C showed no difference from those of unoxidised spheres and neither is there any difference in the appearance of the neck fractures. This
Indicates that the presence of oxide films has no influence on the growth of necks.

Table 14: Neck Diameters measured from Scanning Electron Micrographs

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Sintering Temperature °C</th>
<th>Effective Neck Diameters (microns)</th>
<th>Mean Value d</th>
<th>Standard Deviation σ</th>
<th>d/D</th>
</tr>
</thead>
<tbody>
<tr>
<td>PW 128</td>
<td>825</td>
<td>19, 37, 39, 31, 23, 39, 60</td>
<td>35.4</td>
<td>13.39</td>
<td>0.056</td>
</tr>
<tr>
<td>PW 126</td>
<td>1040</td>
<td>58, 70, 72, 57, 88, 60, 73, 73</td>
<td>68.9</td>
<td>10.34</td>
<td>0.109</td>
</tr>
<tr>
<td>PW 133</td>
<td>1040</td>
<td>Using oxidised spheres 84, 80, 72, 65, 74, 63, 78, 74, 73, 79, 71, 76, 76</td>
<td>74.2</td>
<td>5.78</td>
<td>0.118</td>
</tr>
<tr>
<td>PW 129</td>
<td>1240</td>
<td>111, 129, 127, 77, 104, 141</td>
<td>114.8</td>
<td>22.79</td>
<td>0.182</td>
</tr>
<tr>
<td>PW 134</td>
<td>1424</td>
<td>201, 143, 213, 216, 253</td>
<td>205.2</td>
<td>39.84</td>
<td>0.326</td>
</tr>
</tbody>
</table>

The experimental results of resistance per sphere + neck and diameter ratio, d/D, are plotted and compared with the calculated curves in figure 78. The results fit the lower curve better than that which assumes a cylindrical resistance path through the sphere necks (equation 6.1). However, the 2 models coincide for large neck diameters when the line of spheres does become a cylinder and d/D = 1. At low neck diameters, a small error in measurement of neck diameter would cause a large deviation from the calculated resistance of either model. Another reason for the difference between the observed data and the experimental curve of equations 6.4 and 6.5 may be due to the uncertainty implicit in the model at low...
Figure 78. Comparison of theory & experimental results.
d/D values. In this case, the neck resistance becomes indeterminate in the limit where neck thickness and area approach zero. The resistance would then become infinity x zero. The experimental curve does, however, approach the model curve at values of d/D greater than about 0.1.

In the case of point PW 128, only a few neck measurements were made but most fall within one standard deviation of the mean value. The resistance value is high if the lower line of figure 78 is assumed to be correct. Close examination of the neck micrographs of this specimen, figures 43-48, indicate the high porosity of these necks which would lead to a high diameter ratio for the observed resistance. Figure 47 shows evidence of the specimen being charged by the electron beam suggesting the presence of an insulator which would account for the high resistance value for the observed diameter ratio. If both these affects could be corrected, this point would be moved towards the lower calculated curve of equations 6.4 and 6.5.

The next largest neck size obtained by heating at 1030°C is shown at PW 126 and PW 133, the latter being for oxidised spheres using titanium contacts. Similar resistance values showed that no correction was necessary for reaction with platinum at this temperature. Again, examination of the micrographs, figures 31-39, and figures 58-70, show that the porosity of the neck may have been under-estimated so values of resistance and diameter ratio may be corrected towards the model curve of equations 6.4 and 6.5. The increase in resistance at this temperature as a result of oxide film solution in the case of PW 133 will be very small. The additional 0.02% by weight predicted by the oxidation experiments would cause an increase in resistivity of about 1.5%. Such a small increase would be difficult to detect or attribute to a specific effect.
The next largest neck size was obtained by heating specimens at 1240°C. In the case of PW 129, the reaction between the platinum contacts and the adjoining spheres was extensive forming an intermetallic compound and giving a very high resistance. The experiment was repeated using titanium contact wires PW 135, and the corrected resistance value using d/D for PW 129 was then very close to the calculated curve. The specimen was very brittle and only a few spheres could be preserved for examination, explaining the wide scatter of neck diameter measurements. The resistance value was relatively high and indicated a resistivity approximately twice that of the starting material. Neck porosity seemed to be low so the high resistance may be due to reaction of the specimen with the furnace atmosphere or reaction with the alumina tube as noted earlier.

Some polished sections of spheres were examined in the optical microscope and microhardness tests carried out to estimate the extent of contamination. Using a 20 g load for hardness tests on as-received spheres, a value of 255 VPN was measured. Spheres sintered at 1040°C had a similar hardness value, while those sintered at 1240°C had a hardness of about 450 VPN which suggested the presence of 2-3 atomic percent of oxygen. This is perhaps double that of the as-received material. The oxidised spheres of experiment PW 133 sintered at 1040°C had a hardness of 256 VPN both at the surface and in the core, which suggested complete solution of the oxide film. Spheres sintered at 1424°C (PW 134) had a very high hardness. Using a 50 g load, the surface layers had a value of 800 VPN while the interior hardness was 1200 VPN. Figure 79 showed the core to have
Hardness traverse of spheres sintered at 1040°C
a 2 phase structure, while the outer layers of the sphere had a single phase structure. From the work of Redden & Shamblen((124)) on the variation in hardness of titanium with oxygen content, both values corresponded to an oxygen content of about 10 atomic percent which is in excess of the solid solubility of oxygen in titanium at room temperature. However, if the structure of these spheres is a result of reaction with the alumina tube, this anomaly may be explained. Aluminium is an α-phase stabiliser and a relatively slow diffusing element in titanium. Therefore, in the time available for reaction, it could form a substitutional solid solution in both the surface and core. The stabilised α-phase of the surface would permit the solution of more oxygen to form a single phase structure, while the core material would have a 2 phase structure with the same oxygen content as the surface layer. Although this has little influence on the neck size, the resistance value is very high and use of this formation has not been used for the sintering equation.

Using a 5 g load, hardness traverses were carried out on specimens sintered at lower temperatures to see if there was any gradient of hardness across the necks or between the surface and core of spheres. No definite gradients could be found on any of the specimens so it may be assumed that oxygen becomes uniformly dissolved in the sphere in the time permitted for sintering. A typical hardness traverse is shown in figure 80.

It is now possible to relate the neck measurement data which gives the value of d/D in the resistance equations to the sintering equation since d/D = x/a.
This has been carried out in the following manner:

1. It is assumed that d/D is measured with reasonable accuracy so the ideal value of resistance for a given d/D may be found from the experimental curve of figure 78.

2. The value of d/D as measured from the micrographs is the same as that at the termination of isothermal sintering, i.e. no further sintering takes place during cooling.

3. The experimental results may be normalised for temperature and number of spheres by multiplying them by a factor which is the ratio of the ideal resistance value per sphere for the stated d/D and the resistance of the line of spheres at the end of isothermal sintering.

4. The measured values of resistance during the isothermal sintering stage are multiplied by this ratio to give the room temperature resistance per sphere.

5. The value of d/D at any previous time in the isothermal sintering stage may then be read from the graph (figure 78).

6. This value is then used in the sintering equations so that a plot of log x/a or log d/D against log (time) will give a straight line whose slope is the exponent, n, of the sintering equations.

This procedure has been carried out for experiments PW 126 and PW 135, the results of which are presented in table 15 and from which the sintering curves of figure 81 are obtained.

For the specimen sintered at 1240°C, PW 135, the normalised resistance results were used to give x/a values at different times of the isothermal sintering stage. The results are shown graphically in
Figure 81. Sintering curves.
### Table 15: Sintering Results

<table>
<thead>
<tr>
<th>Time (mins)</th>
<th>Temperature (°C)</th>
<th>Resistance (ohms)</th>
<th>Normalised Resistance (ohms)</th>
<th>x/a Equations 6.4 &amp; 6.5</th>
<th>Experimental Curve</th>
</tr>
</thead>
<tbody>
<tr>
<td>PW 126</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>110</td>
<td>1030</td>
<td>0.8278</td>
<td>0.00361</td>
<td>0.065</td>
<td>0.093</td>
</tr>
<tr>
<td>140</td>
<td></td>
<td>0.8008</td>
<td>0.00349</td>
<td>0.072</td>
<td>0.096</td>
</tr>
<tr>
<td>160</td>
<td></td>
<td>0.7940</td>
<td>0.00346</td>
<td>0.073</td>
<td>0.097</td>
</tr>
<tr>
<td>190</td>
<td></td>
<td>0.7863</td>
<td>0.00343</td>
<td>0.074</td>
<td></td>
</tr>
<tr>
<td>210</td>
<td></td>
<td>0.7834</td>
<td>0.00341</td>
<td>0.075</td>
<td></td>
</tr>
<tr>
<td>240</td>
<td></td>
<td>0.7796</td>
<td>0.00340</td>
<td></td>
<td>0.098</td>
</tr>
</tbody>
</table>

Correction factor = $\frac{0.0034}{0.7796}$, slope $0.12$

| PW 135     |                  |                   |                              |                          |                     |
| 120        | 1240             | 0.09988           | 0.00271                      | 0.142                    | 0.192               |
| 180        |                  | 0.09561           | 0.00260                      | 0.160                    | 0.200               |
| 210        |                  | 0.09398           | 0.00255                      | 0.170                    | 0.202               |
| 240        |                  | 0.09286           | 0.00252                      | 0.177                    | 0.205               |
| 270        |                  | 0.09193           | 0.00250                      | $0.183-d/D$              | 0.207               |

Correction factor = $\frac{0.00250}{0.09193}$, slope $0.33$

- Figure 81. Using the least mean squares method of Appendix II, a straight line of slope 0.33 was obtained. This corresponded to the value predicted by Kuczynski[199] for sintering where vapour transport is the dominant neck growth mechanism.
A line has also been drawn through the experimental points in figure 78, so that the resistance values of the sphere and neck pairs automatically include a correction factor for the solution of oxygen at any time during the sintering stage. This experimental curve has also been used to obtain \( \frac{d}{D} \) values, which were then used in a least squares fit to produce another sintering curve, also shown in figure 81, the slope of which was 0.26. This value is close to that of 0.16 predicted by Coble (107), Rockland (108) and Johnson (99) for neck growth by grain boundary diffusion, and that of 0.14 predicted by Kuczynski (96) and Rockland (108) for a surface diffusion dominated mechanism. A vapour transport mechanism is not likely under these conditions as the vapour pressure of titanium at this temperature is 1.16 mPa \((8.7 \times 10^{-6} \text{ torr})\) using Smithells' data (34) and is not high enough to cause significant material transport.

The value of the slope for spheres sintered at 1030°C was 0.12 and is close to the value of 0.16 predicted by Johnson (99) and Coble (107) for neck growth dominated by grain boundary diffusion, and that of 0.14 predicted by Kuczynski (96) and Rockland (108) for a surface diffusion dominated mechanism. The dilatometer experiments at this temperature show shrinkage which implies a grain boundary dominated mechanism.

Treatment of the results for this specimen using experimental resistance values gave \( \frac{d}{D} \) values, which produced a low value of 0.07 for the slope of the sintering curve. The steep gradient of the curve at this point makes accurate determination of \( \frac{d}{D} \) very difficult.

These analyses were not applied to specimens sintered at higher temperatures for the reason of contamination, as already explained.
At 800°C, the data obtained were not sufficiently precise to permit analysis. The largest value of $d/D$ to be measured was 0.18 which corresponds to a linear shrinkage of about 2%. This is well within the 5% limitation of Johnson's model beyond which the geometric approximations are invalid.

The above results only indicate the sintering mechanisms operating for neck growth. Much more data would be required to calculate apparent diffusion coefficients and hence activation energies for the growth mechanism. This would require experiments at temperature intervals of say 50°C, rather than 200°C and use of a much longer isothermal sintering stage. The present continuous heating process masks the precise moment when sintering starts, and this makes it difficult to obtain a value for the diffusion coefficient. However, this would require a lot more time for experimental work.

### 3-Dimensional Models

An attempt has been made to extrapolate the resistance model for single lines of spheres to 3-dimensional arrays. Resistance measurement of single arrays of spheres have been made and compared with that of a short line of spheres.

The resistance of a line of 3 spheres which were sintered for 3 hours at 1030°C (PW 138) was found to be 0.0239 ohms. This compared with a line of 32 spheres, PW 126, which had a resistance of 0.2476 ohms after a similar sintering treatment. These results gave values of 0.0079 and 0.0077 ohms per sphere respectively, showing the consistency of single line data.

The first array to be considered (PW 132) was a close packed array with a basal plane of 7 spheres, 3 spheres in the 3 central interstices and a top layer of 7 spheres. This was packed in an alumina tube of
approximately 2.0 mm diameter, and as each sphere was of 630 µm diameter, the basal layer was held firmly in position. Electrical contact was made through platinum foils pressed lightly against the compact. The specimen was heat treated at 625°C before sintering at 1030°C for 3 hours. After sintering, the room temperature resistance of this material was 0.0246 ohms. Considering the geometry of this specimen, the 3 spheres of the middle layer are each in contact with 3 spheres in the layers above and below. There are thus 9 parallel paths, in an electrical sense, through which current may flow in this array. The resistance per path is thus $9 \times 0.0246 = 0.2214$ ohms.

A second array (PW 137) consisted of a base layer of 4 spheres, a middle layer of 1 sphere and a top layer of 4 spheres. In this case there are 4 conducting paths. After a similar sintering cycle to the previous specimen, the room temperature resistance of this array was 0.0532 ohms. Hence the resistance of each path is $4 \times 0.0532 = 0.2128$ ohms.

In summary then: $R_{1-1-1} = 0.0239$ ohms  
$R_{4-1-4} = 0.0532$ ohms  
$R_{7-3-7} = 0.0246$ ohms

These 2 values for the resistance of a single path in these arrays are very close to one another but differ from that in a single line of 3 spheres by a factor of 10. In the case of these arrays, there is an effective truncation of some of the spheres so the path length is less than that in the single line where contact is through the north and south poles of the spheres. This would lead one to expect a path resistance for an array to be less than that of the single line.
An alternative approach to these simple 3 dimensional problems is to consider the elements of resistance in each section of the array. For example, the line of spheres consists of 3 spheres and 4 necks in series. If \( R_s \) and \( R_n \) are the sphere and neck resistances respectively, then the total resistance for the line is \( 3R_s + 4R_n \).

In the 4:1:4 array, there are 4 necks in parallel, 4 spheres in parallel, 4 necks in parallel, and a half sphere containing 4 paths followed by a mirror of this arrangement. Hence the total resistance:

\[
R_{414} = 2 \left[ \frac{1}{4}R_n + \frac{1}{4}R_s + \frac{1}{4}R_n + \frac{1}{6}R_s \right] \]
\[
= \frac{3}{4}R_s + R_n
\]

The 7:3:7 array is more complex and can be explained using a simple network. Consider first a segment of the array consisting of one third of the central basal sphere, the 2 mutually contacting basal spheres and half of the sphere located in contact with these in the interstice of the central layer. Figure 82 shows the arrangement and its equivalent circuits.

If a voltage \( V \) is applied then by Kirchhoff's law the sum of emf in each circuit is zero. Hence:

\[
0 = l_1(R_1 + R_5 + R_2) - l_2R_5 - l_3R_2
\]

\[
0 = l_2(R_3 + R_4 + R_5) - l_1R_5 - l_3R_4
\]

\[
V = l_3(R_2 + R_4) - l_1R_2 - l_2R_4
\]
\begin{align*}
R_1 &= \frac{1}{3}R_N \\
R_2 &= 3(R_s + R_N) \\
R_3 &= 5/4R_s + \frac{1}{2}R_N \\
R_4 &= 3/2R_s + R_N \\
R_5 &= \frac{1}{4}(R_s + R_N)
\end{align*}

Figure 8.2: Equivalent circuits of 7:3:7 array
Using the matrix:

\[
\begin{pmatrix}
1 & 1_2 & 1_3 \\
V & -R_2 & -R_4 \\
& (R_1 + R_5 + R_2) & -R_5 & -R_2 \\
& -R_5 & (R_3 + R_4 + R_5) & -R_4
\end{pmatrix}
\]

\[
V = -R_2 \left\{ \frac{R_4 R_5 + R_2 (R_3 + R_4 + R_5)}{R_1 R_3 R_4 + R_1 R_2 R_4 + R_1 R_4 R_5 + R_2 R_3 R_5 + R_3 R_4 R_5 + R_2 R_5 R_4} \right\}
\]

\[
= \left( R_1 + R_2 \right) \left\{ \left( R_1 + R_5 + R_2 \right) (R_3 + R_4 + R_5) - R_5^2 \right\}
\]

\[
R = \frac{V}{I_3} = \frac{R_1 R_2 R_3 + R_1 R_2 R_4 + R_1 R_2 R_5 + R_1 R_3 R_4 + R_1 R_3 R_5 + R_1 R_4 R_5 + R_2 R_3 R_5 + R_2 R_4 R_5 + R_2 R_5 R_4}{R_1 R_3 R_4 + R_1 R_2 R_4 + R_1 R_5 + R_3 R_5 + R_4 R_5 + R_2 R_3 + R_2 R_4 + R_2 R_5}
\]

Hence, when \( V = I \), then the total resistance is given by:

\[
R = \frac{R_1 R_2 (R_3 + R_4 + R_5) + R_2 R_3 R_4 (R_1 + R_2 + R_5) + R_2 R_3 + R_1 R_4 R_5}{R_1 (R_3 + R_4 + R_5) + R_2 (R_3 + R_4 + R_5) + R_3 R_4 + R_4 R_5}
\]
To solve this, let \( R_N = 4X \) and \( R_S = 4Y \).

Therefore:

\[
\begin{align*}
R_1 &= 2X \\
R_2 &= 12(X + Y) \\
R_3 &= 2X + 5Y \\
R_4 &= 4X + 6Y \\
R_5 &= 2X + 2Y
\end{align*}
\]

Substituting these values in the above equation for \( R \):

\[
R = \frac{384X^3 + 1384X^2Y + 1552XY^2 + 480Y^3}{128X^2 + 1332XY + 198Y^2}
\]

which in terms of \( R_S \) and \( R_N \) becomes:

\[
R = \frac{6R_N^3 + 21.625R_N^2R_S + 24.25R_NR_S^2 + 7.5R_S^3}{16R_N^2 + 83.25R_NR_S + 12.375R_S^2}
\]

For the complete 7:3:7 array, there are 3 parallel paths of twice the length having this resistance so the resistance of the array is two-thirds of this value.

Substitution of the theoretical values of \( R_S \) and \( R_N \) obtained using equations 6.4 and 6.5 for \( d/D = 0.07 \) should give values for the resistance of the arrays for the conditions in which they were sintered. Thus:

\[
\begin{align*}
R_{111} &= 0.01146 \text{ ohms} \\
R_{414} &= 0.00275 \text{ ohms} \\
R_{737} &= 0.00137 \text{ ohms}
\end{align*}
\]
Once again, this additive approach takes no account of the effective truncation of the spheres so the resistances of the 3-dimensional arrays will be somewhat lower. The resistances predicted by this analysis and their relative magnitudes were not observed in practice. Unfortunately, time did not permit an investigation of this discrepancy.

The assumption that $R_N$ was small may be erroneous. It is possible that, in the case of the arrays, some reorientation of the spheres is possible as was noted during the sintering of compacts of spheres. This would cause cracking at the necks thus increasing their resistance. This is less likely in the single line where spheres are arranged vertically and where the discrepancy is least (a factor of 2). However, no obvious cracking was observed.

It is thus apparent that application of the resistance model to 3-dimensional arrays is very complicated. Much work remains to be carried out on the interpretation of simple models before this method may be used to examine the sintering of powder compacts.

9. CONCLUSIONS

1. The early work on metal powder manufactured by the hydride-dehydride route has shown that oxide films reduce the density of green powder compacts by a small amount. However, these oxide films dissolve rapidly on heating to $600^\circ\text{C}$, and then do not affect the sintering process at the heating rates examined.

2. Small compacts of spherical particles show that sintering begins at various points in the compact and the reaction is not homogeneous.
A resistance model which may give information about the sintering kinetics can therefore only be applied to simple arrays of spheres.

3. A model has been proposed for the resistance changes during the sintering of a line of spheres and experiments have been carried out using an AC bridge for resistance measurement.

4. The resistance model can be used to indicate the changes of neck geometry during the sintering of a line of spheres and thus produce data for use in sintering equations and hence to deduce the dominant sintering mechanism under certain conditions.

5. Electrical resistance data have been used in the proposed model to determine the mechanism of sintering of titanium at 1030°C and 1240°C. The sintering appears to be controlled by grain boundary diffusion or by surface diffusion while dilatometry indicates the first mechanism to be dominant.
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APPENDIX I

Calculation of Mean and Standard Deviation

The mean $\bar{x}$ is formed using the relationship:

$$\bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i f_i$$

The standard deviation $\sigma$ is given by:

$$\sigma = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (x_i - \bar{x})^2 f_i}$$

where $n$ is the total number of observations.

$x_i$ is the value of the $i^{th}$ observation and $f_i$ the frequency of its occurrence.
APPENDIX II

Calculation of the slope of a curve

The slope \( m \) of a line of the form \( y = mx + c \) is obtained using the following:

\[
m = \frac{\sum xy - \frac{\sum x \sum y}{n}}{\frac{\sum x^2}{n} - \frac{(\sum x)^2}{n}}
\]

where \( x \) and \( y \) are the observed data points and \( n \) is the number of points.