

AN INVESTIGATION INTO SOME OF THE FACTORS
AFFECTING THE SINTERING OF ALUMINA

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ABSTRACT

The present work was carried out to determine the effect of different factors on the sintering of alumina using volume shrinkage as the sintering criteria, and to examine the mechanism of sintering over the temperature range 1200°C to 1950°C . Up to 1450°C this work agrees with the accepted theory of sintering by volume diffusion (shrinkage proportional to time to the power of two fifths), whereas, above 1450°C this work was found to differ from the present-day theories of other workers, by giving a time relationship of a one fifth power. An explanation has been formulated using the concept of an exponential rise in the equilibrium concentration of vacancies present in the crystal lattice affecting the concentration gradient of defects from the particle junctions to the surface.

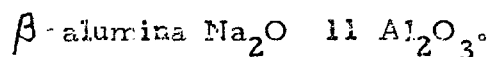
The effect of prefiring at temperatures below that at which sintering begins has been known empirically for some years. The present work explains this behaviour by considering the diffusion of atoms along the surface of the particles to give the formation of necks prior to shrinkage.

Sintering from 1770°C to 1950°C was performed in vacuo, and the temperature range was extended below 1770°C to 1600°C to compare the results with those obtained in air.

The disparity observed has been explained on the basis of evaporation of high-energy areas giving a lower driving force for sintering and subsequent lowering of the shrinkage values compared with sintering in air.

A comparative examination of the effect of particle size and shape indicates the importance of the initial particle size as a control of the degree of sintering.

The effect of additions of 1%, 5%, 10% liquid using sodium silicate as a liquid former, shows that an appreciable amount of liquid is not necessary for liquid-phase sintering, and that for the solution-precipitation stage only enough liquid need be present to form a lens at the particle junctions. With 1% liquid addition no liquid-phase sintering occurs, but enhanced solid state sintering is observed due to formation of



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CONTENTS

Abstract

Acknowledgements

Contents

<u>SECTION I</u> :	Introduction	1
<u>SECTION II</u> :	Survey of the State of Knowledge	3
	Types of bonds in solids	3
	Structures of ideal crystals	4
	Defects in the structure of crystals	5
	Structural Imperfections	6
	Impurity Defects	7
	Lattice Defects	8
	Dislocations	9
	Surfaces and Interfaces	10
	Grain Boundaries	11
	Grain Growth	12
	Factors affecting grain growth	15
	Atomic mobility	15
	Diffusion Processes	17
	Diffusion as an Activated Process	19
	The sintering of oxides	21
	Interaction of surfaces	23

Evaporation-Condensation	23
Surface Diffusion	25
Volume Diffusion	26
Macroscopic Flow	27
Theoretical considerations of sintering	29
Temperature dependence of sintering	33
Defect structures in sintering	34
Effect of particle size	35
Effect of pre-firing	36
Effect of a reactive liquid	36
<u>SECTION III:</u> Plan and Technique of Experiments	38
<u>Experimental Work</u>	
A. Materials	41
B. Sintering Procedures	44
Temperature Measurement and control	47
C. Measurement of Volume of Pellets	52
D. Polished and Thin Sections	52
E. Experimental Procedure	54
Preliminary Work	54
Sensitivity of the Balance	61
Procedure for the Sintering of alumina	63

	Procedure for the sintering of alumina with small additions of reactive liquid	64
<u>SECTION IV:</u>	A. Sources of Error	66
	Temperature Measurement	66
	Time Measurement	67
	Error due to temperature and time	68
	Mercury Balance	69
	Use of Specific Volume	71
	Error due to Losses in Weight	71
	Minimising of Scatter	72
	B. Results and Discussion	74
	1. Solid State Sintering	76
	The effect of Time	76
	Effect of Temperature	84
	Effect of Prefiring on Sintering	87
	Effect of Vacuum on Sintering	90
	Effect of Particle Size	94
	2. Liquid-Phase Sintering	97
	Addition of 1% by Volume of Sodium Silicate	98
	Addition of 5% by Volume of Sodium Silicate	102
	Addition of 10% by Volume of Sodium Silicate	105

References

SECTION 1: INTRODUCTION

The process of sintering is a subject of considerable importance to all industries making components of materials having very high melting points, obviating, for economic reasons, some forming process near these melting points. Sintering is typical of such processes. This part of the industry has gained impetus since the Second World War, although the idea was known for many years before, and qualitative work had been carried out as early as 1922 in Germany⁽¹⁾.

As the quantitative theories appertaining to sintering have only been formulated since 1949, notably by Kuczynski⁽²⁾, Mackenzie and Shuttleworth⁽³⁾ and Clark and White⁽⁴⁾, our understanding of the kinetics of the processes involved is incomplete.

The object of this research was to study the sintering behaviour of alumina, and of alumina with various amounts of sodium silicate as liquid former. This was deemed necessary as additions made by previous workers were either in the range of 20% liquid and upward⁽⁵⁾, or in the very low range, at an impurity level.

Work was begun on the sintering of pure alumina covering the complete range of sintering from 1200°C - 2000°C, as it was noticed that previous work had been in various limited ranges. Certain unexpected features appeared, which caused the simple plan of research to be slightly modified.

SECTION II: SURVEY OF THE STATE OF KNOWLEDGE

To have a fuller understanding of the process of sintering it is necessary to survey the nature of crystals and their defects, as these play an important part in sintering. It is also necessary to know something about the effect of the surface properties of powders on sintering.

Types of Bond in Solids

There are four principal types of bond which occur between atoms in chemical combination, namely, the ionic bond, the covalent bond, the metallic bond, and the Van der Waals' bond.

An ionic bond is one where considerable differences exist in electronegativity between the constituent atoms. It is the result of coulombic attraction of the excess electric charges of oppositely charged ions. NaCl is one example of the ionic bond, which is regarded as a strong bond.

A covalent bond consists essentially of two electrons shared equally between two atoms, one electron being contributed by each atom. This type of bond generally occurs in organic compounds and is present to some extent in

SiO_4^{4-} , CO_3 , and similarly in oxides, MgO , Al_2O_3 , SiO_2 .

A metallic bond is one in which an array of positive ions are bound together in a uniform electron cloud. The bonding energy in this case is much less than that present in ionic bonds.

The Van der Waals' bond is an additional weak electrostatic force between atoms or molecules arising from an interaction of fluctuating dipole moments for the atoms or molecules.

Structures of Ideal Crystals

The bonds between atoms in solids are similar to those already discussed, with the added factor that, in crystals, complex units fit together so as to preserve as far as possible local neutrality and minimise electrostatic forces, allowing solids to have bonds which match at energetically favourable angles and spacings.

As there are four main types of bonding, so there are four types of crystals, each type of bonding imparting particular properties to the crystal.

In ionic crystals, with a similar distribution of electrons as for the ionic bond, an added factor is that positive and negative ions are arranged in a periodic lattice, so that

each positive ion is surrounded by negative ions and vice versa. NaCl is an example of an ionic crystal, the metal oxides being largely ionic in bonding, e.g., MgO, Al_2O_3 .

The bonds in covalent crystals are similar to those of the covalent bonds, a pair of electrons being shared by two atoms. These crystals form when a structure can be built in a repetitive way, consistent with the strong directional properties of the bond. Most crystals have a significant contribution of covalency, an example of a completely covalent crystal being diamond.

Metals are characterised by their particular bond, which has already been described.

When other bonds are absent, then crystals may be formed by Van der Waals' forces, but they form only weak crystals.

With relation to sintering it seems that crystals with ionic or metallic bonds sinter easily, e.g. MgO, Cu, while crystals with a preponderance of covalent bonding are difficult to sinter, e.g. SiC.

Defects in the Structure of Crystals

In an ideal crystal, with no defects present, it can be envisaged that the properties would be very different from

those of real crystals, due to the absence of defects. Growth of such ideal crystals from melts would be almost impossible, as the growth is attributed to steps or defects in their faces, enabling the atoms from the melt to fit into the normal lattice positions, by virtue of the energy of such a surface. Diffusion through an ideal lattice would also be improbable as movement of atoms in such a lattice would necessitate the formation of a defect, the energy of formation of which is enormous. In real crystals, with defects already present, the energy required to move an atom is far less. Higher energies would be required for plastic flow of materials, giving much higher strengths to the ideal crystals compared with real crystals. Defects, therefore, will have a great significance in sintering, particularly those applying to surface regions.

Structural Imperfections

Considering a perfect crystal as one having a completely ordered structure, then a real crystal can be visualised as one having a certain degree of disorder, which can be caused in many ways. The simplest defect one can imagine is the increase in the amplitude of vibrations of atoms about their equilibrium positions as the temperature increases.

Another simple defect is caused by exciting electrons into higher energy bands, leaving electron "holes" or vacant positions in the normally filled electron band. More complex causes of defects are due to impurities, vacant atomic sites, interstitial atoms, by dislocations or line defects, and the boundaries between crystals in an agglomeration.

Impurity Defects

Foreign atoms can be introduced into a crystal structure either by substitution, that is, by replacing a lattice atom, or interstitially, that is by fitting into the interstices between the lattice atoms. If the energy of the system is increased appreciably by the inclusion of a foreign atom, then the crystal system will be unstable, resulting in the rejection of the atom. If the inclusion of the atoms in an ordered way results in a large decrease in the energy of the system then a new stable crystal phase will be formed. Between these extremes atoms may be accommodated in the structure in a random way. For oxides the factors affecting the extent of impurity addition are the relative ion sizes and the valencies of each atom type. In some cases the inclusion of a foreign atom necessitates an associated charge balance so that the electrical neutrality of

the crystal can be maintained. This usually results in the formation of either a cation or an anion vacancy.

Lattice Defects: Even without the inclusion of foreign atoms, several different defects can occur in crystal lattices, the two main defects being the Frenkel defect⁽⁶⁾ and the Schottky defect⁽⁷⁾.

When an atom leaves a lattice site to take up an interstitial position, then the defect formed, having both a vacant lattice site, and an interstitial atom, is called a Frenkel defect. The occurrence of this particular defect increases with temperature, as the entropy or randomness of the crystal is increased, which favours thermodynamic stability.

When an equivalent number of cations and anions leave their lattice sites and build up a new layer on the surface of the crystal, then the defect formed is called a Schottky defect. With this kind of defect there is an increase in the volume of the crystal due to the building up of a new surface. Thus, the main difference between these two kinds of defects is that the Frenkel defect consists of vacant lattice sites and interstitial atoms, whereas the Schottky defect consists of vacant lattice sites only.

Another type of lattice disorder is the Jost⁽⁸⁾ defect where only the interstitial positions are filled, without any

vacant lattice sites. Finally, another disorder occurs with an interchange of positions of two types of atoms, called the place-exchange mechanism.

Dislocations: The preceding paragraph has been concerned with specific lattice position or point defects. Dislocations are defects which occur as line disorders. Unlike point defects, dislocations have no equilibrium concentration which can be calculated by thermodynamics and although their formation is not altogether clear they are believed to be introduced in a non-equilibrium way during solidification, crystal growth or cooling. Another possible source is thermal or mechanical stresses and the precipitation of vacancies during cooling.

Movement of dislocations can best be visualised by the plastic deformation of a material. Dislocations in a crystal can move in one of two ways, the first being movement in the slip plane, which requires only a small stress. The actual slip of one part of a crystal over another occurs by wave-like motion of a dislocation in the slip plane, so that the lattice disturbance is limited to a narrow region around the dislocation, otherwise, the stress required to move one part of a crystal relative to another, disturbing the whole plane

would be far too high⁽⁹⁾. The boundary between the slipped and the unslipped portions of a crystal is called the dislocation line. When the dislocation line is perpendicular to the direction of slip, it is called an edge dislocation, and when it is parallel to the direction of slip, a screw dislocation. The structure of an edge dislocation is equivalent to the insertion of an extra plane of atoms in the crystal. The movement of dislocations in the slip plane is confined to the surface containing the dislocation, whereas the second general type of movement involves the climbing of a dislocation from plane to plane. This process must involve the movement of vacancies and interstitial ions through the lattice and, unlike the slip movement proceeds slowly and at more elevated temperatures. One of the most important aspects of dislocation, as far as chemical action is concerned, is the interaction between dislocations and impurity defects. Since impurity atoms distort the crystal locally, then they must interact with the stress field present at a dislocation⁽¹⁰⁾.

Surfaces and Interfaces: The surfaces and interfaces that exist in a ceramic body are very important in determining many properties of that body. There are two ways in

which surfaces can be thought of. Firstly, they can be regarded as two dimensional imperfections or, secondly, the surfaces of a crystal could be used to define a particular crystal structure in any environment. In either case it is desirable to understand the properties of boundaries or surfaces of a solid or liquid, and the interfaces between phases, as they have such a large effect on the overall processes involved in sintering. Probably the most important effect of a surface is shown in the tendency of either a liquid or solid to form a surface which has the minimum energy.

Grain Boundaries : One of the simplest kinds of interface is the boundary between two crystals of the same kind. If two crystals, having the same orientation are brought together then they will fit together perfectly, but if the crystals are tilted before being brought together, then they will not fit together, but will still be two distinct crystals separated by an interface or a boundary, which is termed the grain boundary. The tilting would produce an interference at the junction of the two crystals, which would be equivalent to a row of edge dislocations. Similarly if the two crystals were rotated, and not tilted before being

brought together, then the interface would be equivalent to a row of screw dislocations at the boundary. As the angle of tilt or rotation is increased there is an increase in the degree of misfit at the boundaries, until at high angles, there would be areas of complete misfit⁽¹¹⁾. This summary of grain boundary properties applies to the ideal case of pure materials. With addition of impurity atoms a segregation to the grain boundaries occurs, because the foreign atoms need not distort the boundaries as much as the lattice in order to fit into the crystal. Another reason is that some atoms may be more stable when fitted in a random boundary than in an ordered lattice.

Grain Growth: The term grain growth and recrystallisation have had a very broad usage in ceramics, and for clarity and precision a clear definition of terms is essential.

Primary recrystallisation is the process by which nucleation and growth of a new generation of strain-free crystals occurs in a matrix which has been plastically deformed.

Grain growth is the process by which the average grain size of a strain-free material increases continuously during heat treatment without change in the grain-size

distribution.

Secondary recrystallisation or discontinuous grain growth is the process by which a few large grains are nucleated and grow at the expense of a fine-grained but essentially strain-free matrix. Although all these processes occur in ceramics, grain-growth and secondary recrystallisation are most commonly encountered, and will now be discussed in further detail.

Grain Growth: It is usually found that an aggregate of fine grains increases in average grain size when it is heated at elevated temperatures. As the average grain size increases it is obvious that the smaller grains must disappear, so that the process of grain growth may be visualized as the disappearance of the smaller grains. The driving force for this grain growth must be associated with the difference in interfacial energy between the small grains and the larger material resulting from the decrease in grain boundary area.

There is a difference of free energy across a curved boundary given by

$$\Delta F = \gamma V \left(\frac{1}{r_1} + \frac{1}{r_2} \right)$$

where ΔF is the change in free energy on going across the curved interface, γ is the boundary energy, V the molar volume, and r_1 and r_2 the principal radii of curvature⁽⁹⁾. This difference in free energy across the boundary is the driving force which makes a boundary move towards its centre of curvature, thus decreasing its curvature. The rate at which a boundary moves is proportional to its curvature and to the rate at which atoms can jump across the boundary.

Secondary Recrystallisation: This process occurs when a small fraction of the grains grow to a large size, absorbing the smaller grained matrix. It is most likely to occur when the normal, continuous grain growth is inhibited by the presence of impurities or pores. Under these conditions, the boundaries that are able to move are those with a curvature much larger than the average, so that they can grow around the inhibiting agents. Secondary recrystallisation also depends on the particle size of the initial powder, a coarse starting material giving a smaller relative growth than a fine material. The driving force for secondary recrystallisation is the lower surface energy

of the large grains compared with the fine grains in the matrix,

Factors affecting grain growth The main factor affecting grain growth is the presence of inhibiting agents, such as inclusions or impurities or pores. A layer of liquid covering the interface also has an inhibiting effect as it reduces the driving force and increases the path of diffusion. Another factor which affects the growth of a crystal is the number of sides it possesses, as this affects the curvature of the sides. For a matrix of equal sized particles, their sides are usually straight and meet at the corners at 120° , because the boundaries would have equal energies. For a two-dimensional picture, this can only occur if the grain has six sides. Grains with less than six sides will have concave sides, viewed from the centre of the grain, while it will be convex for grains with more than six sides. Thus grains with less than six sides will shrink as the boundaries move towards the centres of curvature of the grains.

Atomic mobility: For chemical reactions and microstructural changes to take place in condensed systems, atoms must be able to move about inside the crystal structure. The

simplest to visualize is the direct exchange of two atoms, or by movement of a closed ring of atoms, as the direct exchange of only two atoms is improbable due to the high strain energy necessary. A second process which might take place is the movement of an atom into an adjacent vacant lattice site as these vacant sites are present in every real crystal above absolute zero temperature. The rate of diffusion of atoms by this process depends on the ease of movement of the atoms into a vacant lattice site and on the concentration of these vacant sites. Atomic movement by this process is probably the most common process in atomic mobility. If atoms diffuse one way then the process can be visualized as the movement of vacant lattice sites in the opposite direction, so that this process is commonly called vacancy diffusion.

Another mode of movement of atoms through a lattice is by interstitial atoms. In the formation of Frenkel defects atoms move easily from normal lattice positions to interstitial positions, and the movement of these interstitial atoms through the lattice is another mechanism of movement. Another form of this same process is the movement of an interstitial

atom into a normal lattice position, in which case the "resident" atom is moved out into an interstitial position to make room for the incoming atom. This process can take place even though the movement from one interstitial position to another is unfavourable.

For sintering, in the cases where diffusion is prevalent, then the speed of migration of the atoms will determine the rate of sintering. There are also two possible paths along which diffusing atoms can move. The first is through the bulk of the crystal, commonly called "volume diffusion" and the second along grain boundaries or other such interfaces and surfaces, and called "surface diffusion". The diffusion mechanism plays a very important part in the sintering of oxides, and will be discussed in detail at a later stage.

Diffusion Processes

As the sintering of oxides depends to such a large extent on diffusion it is necessary to consider the laws governing diffusion, without being involved with the rate controlling mechanism.

Fick's Laws: The fact that the rate of diffusion is partly governed by the concentration gradient of the diffusing species

was first put forward by Berthelott. Following his postulation, Fick⁽¹²⁾ formulated a mathematical approach to the problem. Fick's first law states that the quantity of diffusing material which passes per unit time through a unit area normal to the direction of diffusion is proportional to its concentration gradient

$$J = -D \frac{dc}{dx}$$

where J is the actual flow per unit time per unit area, c the concentration per unit volume and x the direction of diffusion. The constant of proportionality in the equation, D , is termed the diffusion coefficient, and is expressed in units of square centimetres per second.

This equation gives the rate of diffusion of a steady flow across a unit area in terms of the concentration gradient of the diffusing species. Similarly, the relationship between the change of concentration and time may be expressed in the equational form of Fick's second law of diffusion

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2}$$

This equation refers to the unsteady state of flow. The main criterion of Fick's Laws being that the material will only flow if there is a concentration gradient of the diffusing species

between the two particular points. If the material is perfectly homogeneous, with no concentration gradient of any kind, then there can be no net transfer of atoms to or from any particular point. Another way of stating this driving force is that all concentration gradients tend to be evened out. Some investigators⁽¹³⁾ have, however, considered diffusion not on the basis of a concentration gradient, but that it is a function of the activity gradient.

Diffusion as an Activated Process

On closer examination of the diffusion coefficient, D , there is no reason why it should be assumed to be constant, since there is a distribution of energy through the lattice, dependent on its defect state, which varies with temperature. There is also an energy barrier which must be surmounted for a migration of ions from normal sites to either interstitial positions or to vacant lattice sites. Furthermore, any local variation in composition or defect types will cause variation in the same way. When dislocations occur in the lattice, the importance of this aspect cannot be neglected. The energy which must be supplied to the atoms to surmount the energy barrier between the lattice position is called the activation energy for the process. As the temperature of

the system is increased the fraction of atoms which has sufficient energy to surmount the energy barrier also increases; also, the number of defects increases⁽¹⁴⁾, the overall increase being exponential, so that the temperature dependence of the diffusion coefficient is given by an Arrhenius type of equation

$$D = D_0 e^{-E/RT}$$

where D = diffusion coefficient; D_0 = a constant or a pre-exponential factor; E = Activation energy; R = gas constant; T = absolute temperature.

The Arrhenius plot gives the relationship between the diffusion rate, the temperature of the diffusion, and the activation energy for the process at that temperature. The values of D_0 and E are of great importance in establishing the mechanism controlling the process.

The Sintering of Oxides

Essentially the process of sintering must initially involve the interaction of the surface atoms on particles which touch, followed by the rearrangement of the bonds across the boundary. After this stage there must be transfer of material across this region by one or more of several possible mechanisms. It is probable that all the mechanisms make some contribution to this transfer, possibly several of them simultaneously, under certain conditions, and that the present theories on sintering are qualitative approximations. It seems feasible that by changing the conditions of the environment the rate controlling mechanism can be changed, so that every possible mechanism is potentially the governing process.

The sintering process is fundamentally dependent on the requirement that an equilibrium system shall achieve the maximum state of order and the minimum free energy, so that in the course of the process there is a general increase in order, and a reduction in surface free energy by the reduction of the total surface area.

With an idealised material the aspects which may be considered to be of major importance in affecting the sintering behaviour of this material are:

- (1) Interaction of bonds between adjacent particles;
- (2) Evaporation and condensation of material;
- (3) Surface diffusion of atoms into the region of the contact area;
- (4) Transfer of material to the contact area by volume diffusion;
- (5) Macroscopic flow of material, especially in the presence of high mechanical stresses applied to the material;
- (6) Grain growth.

These points are of fundamental importance in the sintering process, but there are other factors which play an important part in the sintering behaviour of any particular material, such as:

- (1) The effect of particle size, shape and distribution;
- (2) The disappearance of both open and closed pores;
- (3) The effect of the gas atmosphere surrounding the material.

In order to minimise the variables encountered in the sintering process most of the fundamental work done in the field has been carried out on simple systems and comparing experimental results with these systems ^(2,4).

As the driving force for the system is the same in all cases (the minimising of surface free energy) then differences in behaviour in the various types of systems will be dependent on the overall mechanism of material transfer, which is in operation in each case, so that a theoretical knowledge of the several possible mechanisms will be of use in the later discussion.

Interaction of surfaces: Even though little is known of the chemical or physical bonds between adjacent solid surfaces, it has been well established that these bonds are modified significantly by the defect nature of the surface region, and that adsorbed gases on the surface affect the kinetics of the sintering process. The greater the disorder in the surface, the greater will be the tendency for the surface to surface bonds to intersect, due to the high surface energy of a disordered solid⁽¹⁵⁾. The bond interaction will also be greatly affected by the presence of another phase between the two surfaces.

Evaporation-Condensation: This mechanism is the easiest to treat quantitatively, but is dismissed by most authors as being too limited in its application. When it is considered, however, that the vapour pressures surrounding the grain are

considerably higher⁽¹⁶⁾ than those deduced from high temperature equilibrium measurements, then this mechanism becomes feasible, e.g. NaCl.

This process of material transfer depends on the difference in vapour pressures above the free surface of a particle and the junctions of two adjacent particles. It is known that the vapour pressure above curved surfaces is dependent on the radius of curvature of the surface. Thus the vapour pressure above a positive curvature (concave when viewed from inside a grain) is greater than above a plane surface which in turn is greater than the pressure above a negative curvature (convex when viewed from inside the grain). As the free surface of a spherical grain has a positive curvature and the junction between adjacent grains a negative curvature, it is evident that there will be a "pressure gradient" between the two regions, resulting in the transfer of material from the free surface to the junction. This results in a build up of material around the junction or "neck", (in future referred to as a neck-growth), and it is evident that the phenomenon is a transfer of materials from surfaces and not from the body of the particle, which means that there will be no change in the distance between particle centres, or in

other words, there will be a change in pore shape, but no densification or removal of pores⁽¹⁷⁾.

Surface Diffusion: Tammann⁽¹⁸⁾ has shown that at temperatures greater than approximately half of the melting temperature ($^{\circ}\text{K}$) - commonly referred to as the Tamman temperature - lattice mobility becomes appreciable, whereas below this temperature it is negligible. However, Nüttig⁽¹⁵⁾ has shown that surface mobility is appreciable down to a fifth of the melting temperature, or even lower, and that this mobility increases rapidly with temperature as does the depth of the surface layer in which it operates. It is however not fully appreciated that the effect of surface diffusion will still persist above the Tammann temperature, although it may be masked by the lattice mobility, and that it probably plays a very important part in the formation of necks in the early stages of sintering.

Another fact which should be borne in mind is that grain-boundary diffusion is but a modification of surface diffusion, and the importance of it cannot be overlooked.

The mechanism of surface diffusion is very similar to that of evaporation-condensation in that material is transferred from the free surfaces of the grains to the surface at the junction of adjoining particles. Whereas evaporation-

condensation relies on the transfer through a vapour phase, surface diffusion relies on the transfer across the surface of the particles, as there is a concentration gradient of surface defects, which tend to be evened out. In the free surface of the particle, there is a disordered structure due to the peculiar nature of the surface, as has been described before. This provides the mobility in the surface which must be present before any diffusion or transfer of material can take place. The difference in free energy or chemical potential between the neck area and the surface of the particle then provides the driving force necessary for diffusion to take place. Again, as this is a surface phenomenon, there can be no densification of material, merely a change of pore shape.

Volume Diffusion: Above the Tammann temperature, spontaneous production of vacancies and lattice mobility occurs, thus facilitating the phenomenon of volume diffusion. From another viewpoint, it is the stage at which the depth of the surface active region has reached the centre of the grain and the "surface" becomes the whole lattice. It is, however, unlikely that material is transferred from the middle of the grain to the surface, as this process would be far too slow to explain the experimental rates observed⁽³⁾. The path for

the transfer of material must be small to give a satisfactory explanation, and the view is that material is transferred from the junction of the particles to the neck-area, or in other words, from a grain boundary to the neck via the interior of the grain. This is synonymous with the diffusion of vacancies from the neck area into the particle junction. The driving force is then the difference in chemical potential between the disordered grain boundary and the "completely disordered vapour phase". Material will diffuse outwards from the junction to the necks, or, in other words, vacancies will diffuse in from the necks to the grain boundary. As this mechanism entails the removal of material from the boundary, the two particles will tend to merge one into the other, as the necks grow, giving a densification and a decrease in pore size.

Theoretically this process could proceed to theoretical density, with no porosity at all, but practically this does not occur as the pores tend to become isolated and with the occurrence of grain growth, the path from pores (vacancy source) to the grain boundaries (vacancy sink) tend to become larger, thus slowing down the whole process until it eventually stops.

Macroscopic Flow: Frenkel⁽¹⁹⁾ was the first investigator to make a serious attempt to develop a theory of sintering. His assumption was that the process consisted of a slow

deformation of the grain under the action of surface tension, which reduces to a Newtonian flow of material from the grain to the neck areas. According to Frankel this flow is due to the diffusion of the holes or vacancies in the lattice. This mechanism of macroscopic flow was later developed^(3,4) to bring in both types of bulk flow, namely viscous flow and plastic flow.

For glasses, which are envisaged as super-cooled liquids, a viscous flow mechanism is generally accepted as being in operation during sintering, in which the surface tension of the particles at high temperatures produce the shearing of planes of atoms, and which gives direct proportionality between shear stress and shear strain.

For crystalline materials the flow takes place plastically, with a well defined yield point. This type of flow is generally referred to as Bingham flow. The characteristic of this type of flow is that the shear stress is proportional to the shear strain only above this yield point.

Although there is considerable information on the deformation of metals, and the related flow mechanisms operating, less information is available concerning ionic crystals, but it is accepted that the flow of material is similar

to that of metals, so that the plastic flow would take place, in low temperature regions by slip or glide along preferred crystallographic directions and that this slip is associated with dislocations and their "wave-like" movement through the crystal.

Besides plastic deformation, another possible mechanism of plastic flow would be that of creep, in which stress above a certain limit but below the breaking stress gives elastic deformation followed by a zone for which the deformation is proportional to time. This steady flow stage is generally referred to as viscous flow, but is not Newtonian flow as the flow rate does not increase proportionally with stress.

Theoretical Considerations of Sintering

The first attempt to formulate a theoretical concept was made by Sauerwald⁽¹⁾ who postulated that during sintering there existed two distinct stages. Firstly, adhesion occurred due to the mutual attraction of surface atoms, and surface tension. On reaching a certain characteristic temperature (which he put down as three quarters of the absolute melting point) rapid shrinking is caused by spontaneous interchange of atoms between adjacent particles, called crystallisation, and is the second stage of sintering. Hüttig

et al⁽²⁰⁾ from 1941 to 1948 carried out extensive research on sintering and gave individual temperature zones a particular characteristic:

- (1) First temperature range 0-0.23 of absolute melting point
Period of adherence of particles;
- (2) Second temperature range 0.23-0.36 of absolute melting point
Period of surface diffusion;
- (3) Third temperature range 0.33-0.45 of absolute melting point
Period of grain boundary displacements by growth;
- (4) Fourth temperature range 0.37-0.53 of absolute melting point
Period of lattice diffusion;
- (5) Fifth temperature range 0.43-0.8 of absolute melting point
Period of formation of new crystallisation centres;
- (6) Sixth temperature range 0.8-1 of absolute melting point
Period of excessive grain growth.

This gives good agreement with present day theories.

Frenkel⁽¹⁹⁾ advanced a theory based on work carried out by Balke⁽²¹⁾, and postulated that the sintering of metallic particles is caused by surface tension forces, in which metals can display a viscous flow similar to amorphous solids. This flow is due to the diffusion of cavities of an atomic order of magnitude, in contrast to the ordinary plastic flow of the

particular metal. His work was closely followed by Shaler and Wulff⁽²²⁾, but in neither case was the theory validated by conclusive experimental work.

Mackenzie and Shuttleworth⁽³⁾ favoured the mechanism of plastic or viscous flow for sintering, using as their model a single spherical pore in a solid medium surrounded by a composite material containing a uniform distribution of holes. The later stage of sintering was considered when all open pores have disappeared and the remaining pores surrounded by a solid matrix. The material was visualised as flowing into the pores, which are under a positive pressure from the gas within them. Their experimental work agreed well with the theory, for the latter stages of sintering, but some discrepancy occurred during the initial stages.

Clark and White⁽⁴⁾ considered the initial stages of sintering when the pores are open, giving a continuous matrix of the gas phase. Their model was taken as two spheres in contact, with surface tension forces operating to give plastic flow of the material to the neck areas of the particles in contact. However, to fit their experimental results to the theoretical curves several empirical correction factors had to be incorporated in the formulae, based mainly on the difference in geometry

between the model and the real compact.

Kuczynski's⁽²⁾ theoretical considerations were based on almost the same model as that of Clark and White, with the difference that he considered a single sphere being sintered on to a flat plate. His theory was concerned with the time dependence of sintering, but unlike Clark and White, whose theoretical model was the idea of two spheres in contact, and whose measurements were made on compacts of irregular-shaped powders, Kuczynski's practical work was carried out on spheres of copper being sintered on to a flat copper plate, the measurement taken being that of the increase in neck diameter. He showed mathematically that different mechanisms would give different time dependencies, e.g.

$\frac{x^5}{a^2} \propto t$	Volume diffusion
$\frac{x^7}{a^3} \propto t$	Surface diffusion
$\frac{x^2}{a} \propto t$	Viscous or plastic flow
$\frac{x^3}{a} \propto t$	Evaporation and condensation

where x = neck diameter, a = radius of spherical particle,
 t = time of sintering.

By plotting the increase in neck diameter against time on a logarithmic scale he showed that the slope of the straight lines produced agreed with a volume diffusion mechanism.

Although Kuczynski's mathematical treatment has been criticised, the general conclusion reached by many authors^(5,17,23) is that the rate controlling mechanism for solid state sintering is that of volume diffusion, although it is also believed⁽²⁴⁾ that at the onset of sintering surface diffusion occurs to start off the growth of the necks.

Temperature dependence of sintering

As diffusion is an activated process, obeying the Arrhenius equation

$$D = D_0 e^{-E/RT}$$

then if sintering is wholly dependent on the diffusion of lattice ions through the body of the crystal, on the surface diffusion of atoms or on grain boundary diffusion, then sintering could be described as an activated process, and could be designated an energy of activation, i.e.:

$$\text{Rate of sintering} = A_s e^{-E_s/RT}$$

where A_s = a constant, E_s = activation energy for sintering, R = gas constant and T the absolute temperature.

A plot of the logarithm of the change of volume against reciprocal temperature of sintering ($^{\circ}\text{K}$) should then indicate the dependence of sintering on volume diffusion, i.e. an activation energy comparable to that of volume diffusion should be calculable.

Defect Structures in sintering

Although most investigators have worked on establishing one of the many possible mechanisms as the rate controlling process in sintering, little work has been done to establish what ions or group of ions are in fact determining this rate process. Before any exact evaluation of the mechanisms involved can be made, the mode of transport and the nature of the ions moving must be firmly established, as it seems very likely that a difference in the defect nature of the solid will change the diffusion condition and, therefore, the possible mechanism for sintering.

Effect of gas atmosphere

In considering the effect of defect structure on the sintering process, the effect of the gas atmosphere cannot be neglected. The gas phase surrounding a surface can change

the defect structure of this surface very considerably, and thus the sintering process itself. It must also be borne in mind that a change in gas atmosphere could affect the transport mechanism by affecting the vapour pressure of the solid, and possibly promoting the evaporation-condensation mechanism. Schottky and Wagner⁽²⁵⁾ have described the equilibrium set up between the gas phase and the lattice defects in a solid, while Gray⁽²⁶⁾ discusses the adsorption and desorption of gases on the surface of solids affecting the defect structure.

Effect of particle size

As the size of particles increases, the number of particle contacts decreases, and the distance travelled by the ions from the lattice sites to the neck areas also increases. It has been experimentally shown by Coble⁽²⁷⁾ that the rate of neck-growth between particles decreases logarithmically with the particle size, over a very wide range of particle diameters.

It is also known that grading of powders to different distribution of coarse, medium and fine fractions can change the final densities achieved in a sintered body. It is therefore evident that for a fair comparison of sintering characteristics the same particle size distribution must be maintained throughout the experimental work.

Effect of pre-firing

Assuming that surface diffusion is the initial mechanism in sintering, then pre-firing specimens before the actual sintering process should give different areas of contact between particles which should show in the total amount of shrinkage taking place during the actual firing of the specimens.

As surface diffusion gives no volume shrinkage of the pellets, pre-firing at temperatures below that at which shrinkage begins, i.e. 1150°C for Al_2O_3 , should enable a correlation to be carried out between the actual shrinkage on sintering and the extent of surface diffusion to form necks at various temperatures, and thus establish the role played by surface diffusion in sintering.

Effect of a reactive-liquid

Most of the work carried out on sintering in the presence of a liquid phase has been on the addition of relatively large ($> 10\%$) fractions of liquid former⁽⁵⁾. With such an appreciable amount of liquid present the process of sintering can be considered in three stages⁽²⁸⁾:

- (a) The rearrangement of the solid particles in the liquid matrix to give a more dense body;
- (b) Solution of solid at the points of contact and reprecipitation at the neck. There is increased

solubility at the points of contact due to the surface tension forces between the particles;

- (c) Sintering slowing down due to the formation of a solid skeleton.

With small liquid additions the effect of the rearrangement process will be very small compared with the solution precipitation process and the rate controlling factor should be the diffusion of the solute ions to the neck. Interaction of the liquid with the surface of the particles may also affect the defect structure of the surface giving enhanced surface mobility. If the solid particles are sufficiently small then this effect could well be evident in the bulk of the particle as well as the surface.

The liquid may also affect the growth properties of the solid, by forming a layer between the particles, thus inhibiting the movement of the boundary from one surface to another, this would ensure the removal of the pores from around the particles to give a dense compact.

SECTION III: PLAN AND TECHNIQUE OF EXPERIMENTS

The sintering of a powder compact changes many of its physical properties, so that a variety of techniques have been used in the past to determine the sintering behaviour of the different powders. Model experiments have also been devised to minimise the variables encountered in the sintering process, and these have been extremely useful in formulating the theories of the sintering mechanism.

Kuczynski⁽²⁾ in his model experiments sintered spheres of copper to a copper plate and measured the growth of the necks with a microscope. He extended his experiments⁽²⁹⁾ to considering the sintering of spheres together, the materials used being sapphire, glass and copper. Another variant on this model experiment was the sintering of wires, wound around a bobbin in several layers.

Kingery and Berg⁽¹⁷⁾ also followed the sintering phenomenon by observing the sintering of spheres together in a furnace through a transparent window.

For metals, the sintering behaviour has been followed by measurements of electrical resistivity, magnetic measurements and tensile strengths. For ceramic materials,

excepting ferrites, these measurements offer some difficulty, so that experimental techniques have been rather limited,

Kingery⁽²⁸⁾ has favoured the direct measurement of linear shrinkage by observing compacts in a furnace, using a travelling microscope, while Oel⁽³⁰⁾ has made dilatometric measurements to follow the sintering behaviour of loose powders.

Clark and White⁽⁴⁾ measured the volume shrinkage of powder compacts using a mercury balance, based on Archimedes' principle. This is an accurate method of measuring volume shrinkages and which is quite simple to use.

This last method of measuring volume shrinkage was thought to be best suited for this research and was adopted for the experimental work carried out. It is also the most obvious difference which is seen in sintering, and which needs the closest control possible in industry.

Al - Alumina was chosen as the powder for the research as it was easily obtainable in a very pure form, and has no phase transformations on heating or cooling.

Sodium silicate was chosen as the liquid former as its behaviour in contact with alumina is well known after the work carried out by various investigators in this laboratory⁽³¹⁾.

The $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ system would have been best suited for

this research, being much in evidence in industry, but as most of the components have high melting points ($> 1300^{\circ}\text{C}$) the lower melting (1088°C) sodium silicate was chosen as the best substitute.

Volume shrinkages of alumina compacts and of alumina with sodium silicate additions, were then carried out to determine the effects of temperature from 1200°C - 2000°C , of liquid-forming additions, from 1 - 10%, of gas atmosphere (vacuum and air) and of time on the sintering behaviour of alumina.

Experimental Work

A. Materials

1. Alumina

For the main part of the research "Analar" reagent alumina was used. For a comparative experiment high purity alumina obtained from the Plessey Company was used.

2. Sodium Silicate

This was prepared by fusing "Analar" reagent sodium carbonate and silica in the form of Loch Aline sand in a platinum pot at 1100°C . The powders were thoroughly mixed, with 5% more sodium carbonate than theoretically needed, to make up for loss by evaporation. The liquid silicate was poured out onto an iron plate and powdered when cold. This was then remelted and the process repeated to ensure homogeneity. The powder was kept in a dessicator to avoid moisture pick-up, and used as required.

3. Preparation of Alumina Powders

The powders which were not recalcined were ground in an electrically driven agate mortar for four hours until the particle size was approximately 1-2 microns, a rough check being done with a microscope. The comparative purities of both powders after grinding are shown in Table 1, page 42

TABLE I

Impurity	Analar Alumina	Plessey Alumina
SiO ₂	0.04%	0.02%
Cl	0.005%	0.005%
SO ₄	0.01%	0
Fe	0.01%	200 ppm
others	trace	trace

A more accurate analysis of the particle size distribution was made using the Andreasen pipette method.

For liquid-phase sintering, the Analar powder was used, the silicate powder being added to the ground alumina and thoroughly mixed for half an hour in a tumbling mill.

No other treatment was given to the powders before being pressed into pellets.

4. Mould Used

The mould used for pressing the pellets used in this research project was made from a solid block of Perspex. A half inch hole was drilled, and two fitting Perspex punches made. Perspex was chosen for the mould material as it would minimise the pick-up of inorganic impurities during the pressing operation. The pressures involved were then limited, to increase the life of the mould and a pressure of 0.75 tons per sq. in. was used throughout.

5. Preparation of Pellets

Approximately 1 gram of powder was used for each pellet to minimise variation in pressing stresses and to achieve a fairly uniform initial bulk density. A drop of 10% gum tragacanth solution was added to each sample before pressing to give good green strength to the pellets. The pellets were

then kept in a dessicator for a few hours before use.

B. Sintering Procedures

Furnaces

A platinum-wound horizontal electric resistance furnace was used for temperatures up to 1400°C and open to the atmosphere. This furnace had a $1\frac{1}{2}$ " internal diameter alumina tube. The furnace and controller is shown in Fig. 1, page 45 .

A temperature distribution of $\pm 2^{\circ}\text{C}$ over $1\frac{1}{2}$ ins. at 1400°C was observed for this furnace, and all sintering work was carried out in this zone.

A horizontal furnace with molybdenum tape wound on an impermeable alumina tube was used for temperatures up to 1770°C and open to the atmosphere. An inert gas atmosphere was maintained around the molybdenum winding by using cracked ammonia. The apparatus is shown in Fig. 2, page 46 .

A temperature distribution of $\pm 2^{\circ}\text{C}$ over 3 ins. at 1700°C was obtained with this furnace which was used for the sintering work.

A vertical tungsten element (later changed to molybdenum)

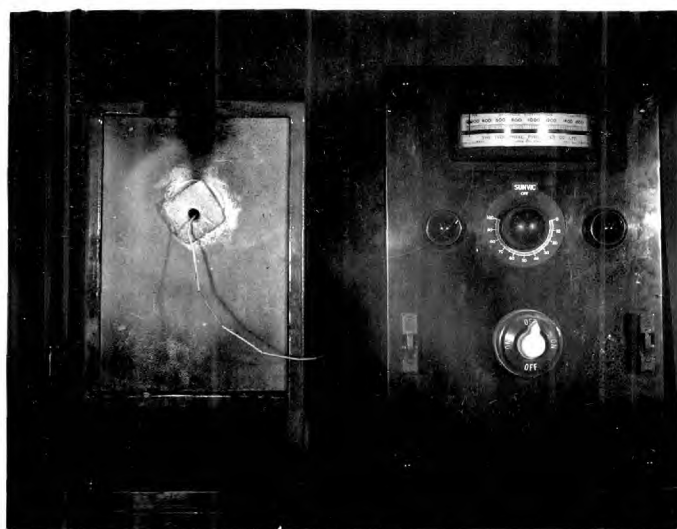


FIG. 1 Platinum wound furnace.



FIG. 2 Molybdenum wound furnace.

vacuum furnace was used for temperatures up to 2000°C , and for comparing sintering experiments in vacuo at lower temperatures ($1600 - 1750^{\circ}\text{C}$) with those conducted in air in the molybdenum wound furnace. The apparatus is shown in Fig. 3, page 48, and a cross section of the furnace chamber in Fig. 4, page 49.

The hot zone was not determined for this furnace, but direct temperature readings of the top surface of one of the specimens was taken with an optical pyrometer.

Fluctuation in the mains A.C. supply was reduced to about one-tenth by a "Regavolt" automatic voltage controller permanently connected in the line for the molybdenum wound furnace and the vacuum furnace.

Temperature Measurement and Control

For temperatures up to 1550°C a platinum-platinum 13% Rhodium thermocouple was used, which was standardised against a standard thermocouple. Above 1300°C , spot readings only were taken, to lengthen the life of this thermocouple. The thermocouple was attached to a potentiometer for accurate temperature readings $\pm 1^{\circ}\text{C}$.

Above 1550°C , when preferential volatilisation of rhodium becomes appreciable, an optical pyrometer was used,

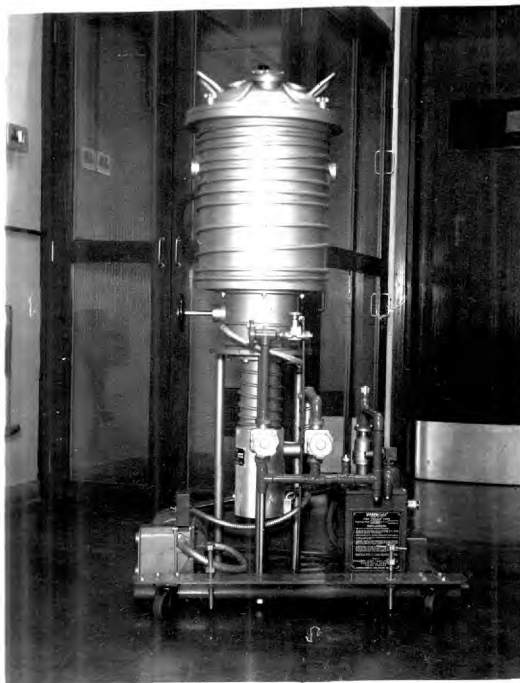
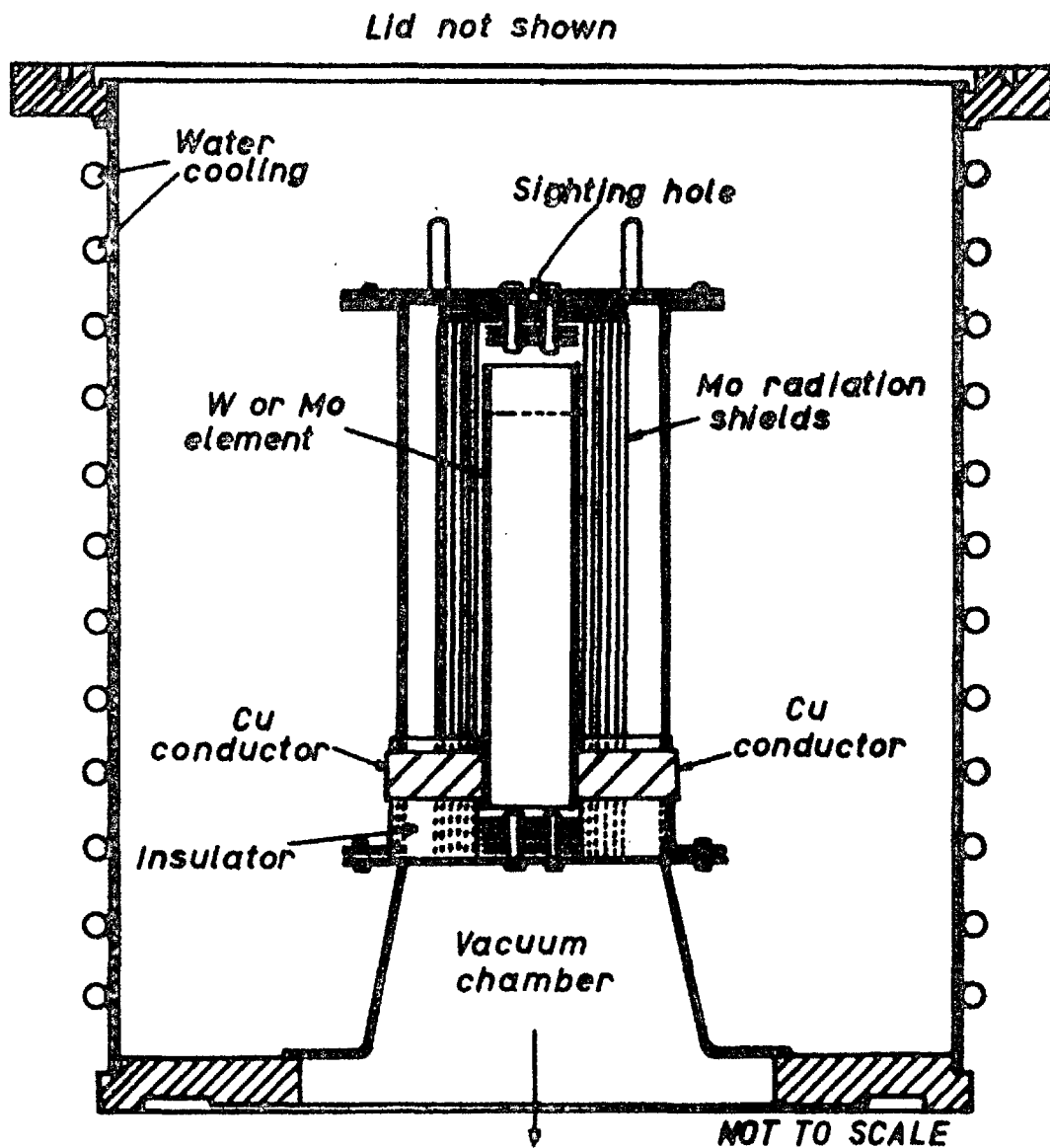


FIG. 3 Vacuum furnace.



VERTICAL CROSS SECTION OF THE
VACUUM FURNACE

Fig. 4

which was accurate to $\pm 10^{\circ}\text{C}$.

The platinum and molybdenum wound furnaces were kept at temperature throughout the experiments, the specimens being pushed into position on permeable alumina boats, 2-3 ins. long.

The boats were pushed slowly into the furnace until they reached a pre-determined position in the hot-zone. The time taken to reach this position was standardised at each temperature to avoid any discrepancy due to unequal heating of specimens. The time for each run was taken from the moment that the specimens reached the hot-zone until the moment they were removed from it.

For the vacuum furnace, an entirely different procedure of heating control was used, because of the nature of the furnace. The pellets were placed in a molybdenum crucible which fitted over a molybdenum pedestal in the furnace chamber. The furnace was then evacuated by a rotary pump to 1 mm Hg pressure, and then to 0.01 microns Hg pressure by an oil diffusion pump. The current was then switched on and the chamber brought up to temperature in about 10 minutes, continual readings of the temperature of the specimens being taken. When the specimen reached the required temperature, the timing of

the run was started. At the end of the run, the current was switched off and the chamber allowed to cool before removing the specimens.

The temperature was measured with an optical pyrometer to $\pm 10^{\circ}\text{C}$, through an adjustable mirror and the silica-glass viewing window on top of the furnace. The optical readings were taken on the specimen in the holder, the pyrometer being calibrated beforehand for absorption loss through the window and mirror.

Control: The platinum-wound furnace was controlled by a "Sunvic" on-off control which regulates the energy input to the furnace by timing the period for which the current is switched on and switched off. This gives a very steady temperature of $\pm 2^{\circ}\text{C}$.

The molybdenum-wound furnace was controlled through a step-down transformer, operated by hand. This again gave a very steady temperature.

The vacuum furnace was controlled through a low-voltage transformer and even with manual control the temperature of the specimens could be reproduced to within the accuracy of the optical pyrometer.

C. Measurement of Volume of Pellets

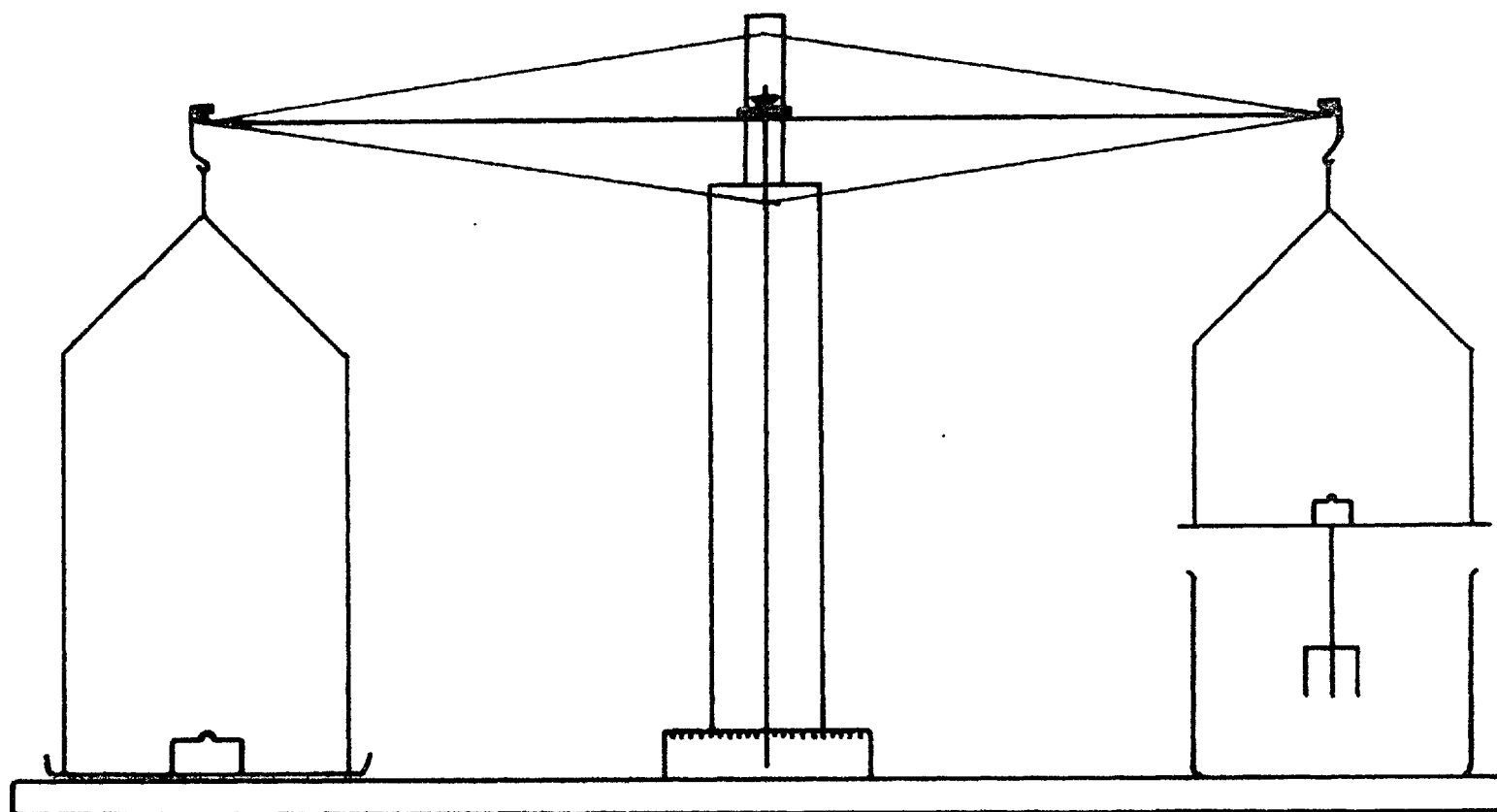
The volume of the specimens were measured by using the simple Archimedes' Principle. The method used by Clark and White⁽⁴⁾ was modified for greater accuracy.

The apparatus, shown in Fig. 5, page 53 consists of an ordinary two-pan balance, one pan being modified for lowering the specimen into the mercury with a grab made of lacquered iron wire.

D. Polished and Thin Sections

In preliminary investigations on polishing, many alternatives were tried, including the use of diamond dust on photographic paper, and a whole range of abrasive and polishing powders. The best results, using a series of diamond dusts on a polishing wheel took about six hours for one specimen, so that this technique was not used.

Thin sections were more readily prepared with the facilities at hand, and they were used in microscopical work.



NOT TO SCALE

MERCURY BALANCE

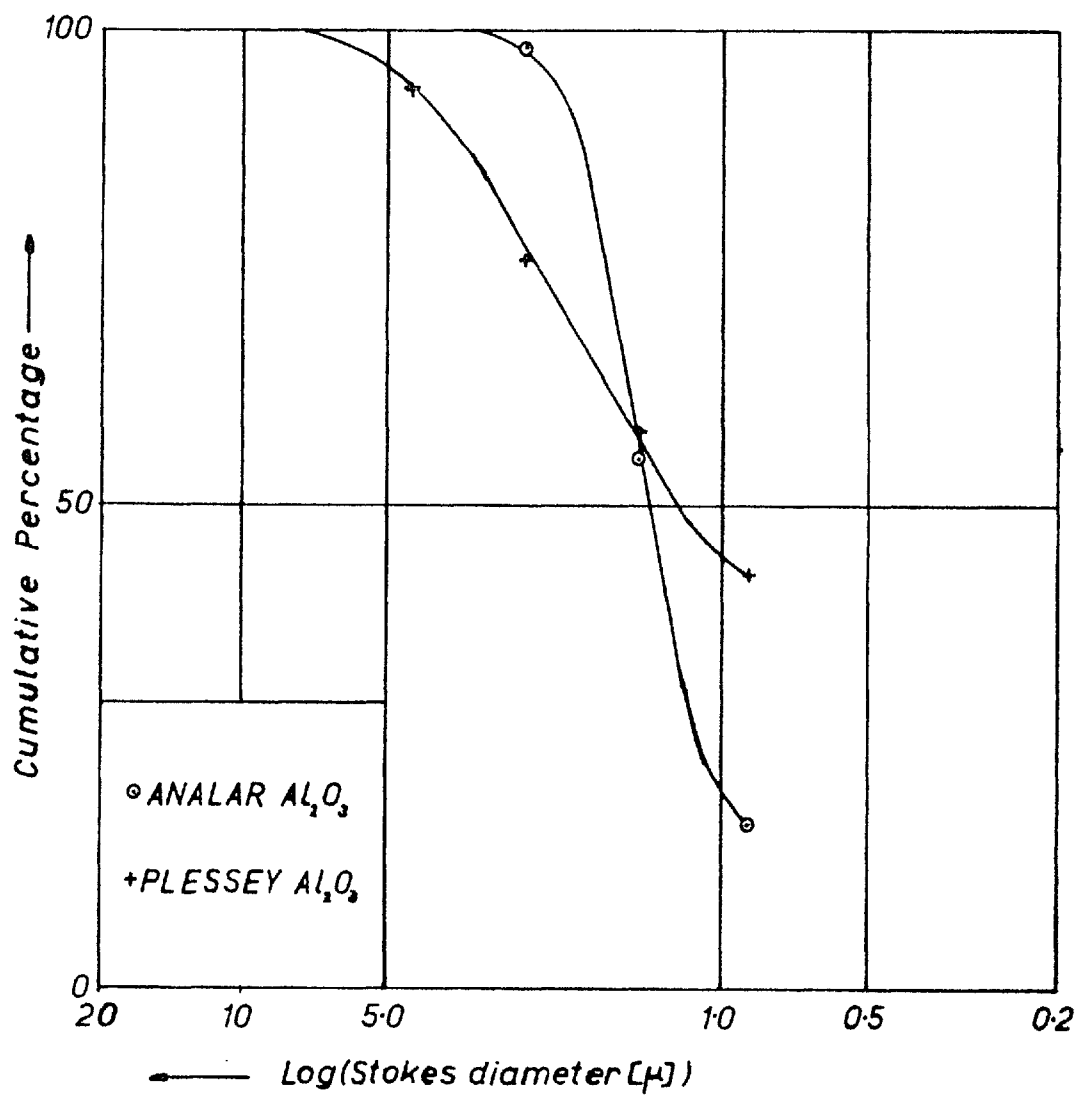
Fig. 5

E. Experimental Procedure

Sintering of Alumina

Preliminary Work: In order to standardize experimental techniques and to calibrate the mercury balance, some preliminary experiments were undertaken on the alumina powder used,

The powder was first of all ground in a power-driven agate mortar for times ranging from 1 hour to 4 hours. It was found that the closest distribution of particle size was obtained by grinding for 4 hours, and this time was then taken as the standard for all subsequent grinding of the "Analar" alumina. The Andreassen distribution curve is given in Fig. 6, page 55. For the Plessey alumina a time of $1\frac{1}{2}$ hours was found to be best, as the distribution curve shown in the same figure was the closest approximation to the other powders obtained. The difference in the two curves was due to the different starting conditions of powder shape and size, shown in the electron microscope photograph, Fig. 7, page 56. Any subsequent operations on the Plessey alumina did not give a better distribution, so that it was decided to use the powder only as a comparison with the "Analar" alumina, which was in greater supply.



Particle Size Distribution of Alumina
Powders

Fig. 6



FIG. 7a Electronmicrograph of 'Analar' Alumina
ground for 4 hrs. (X 2,000)

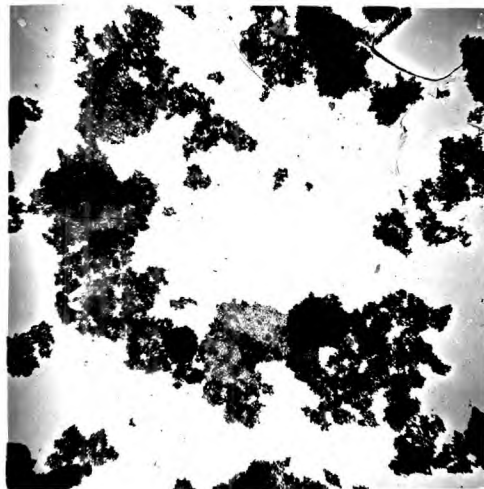
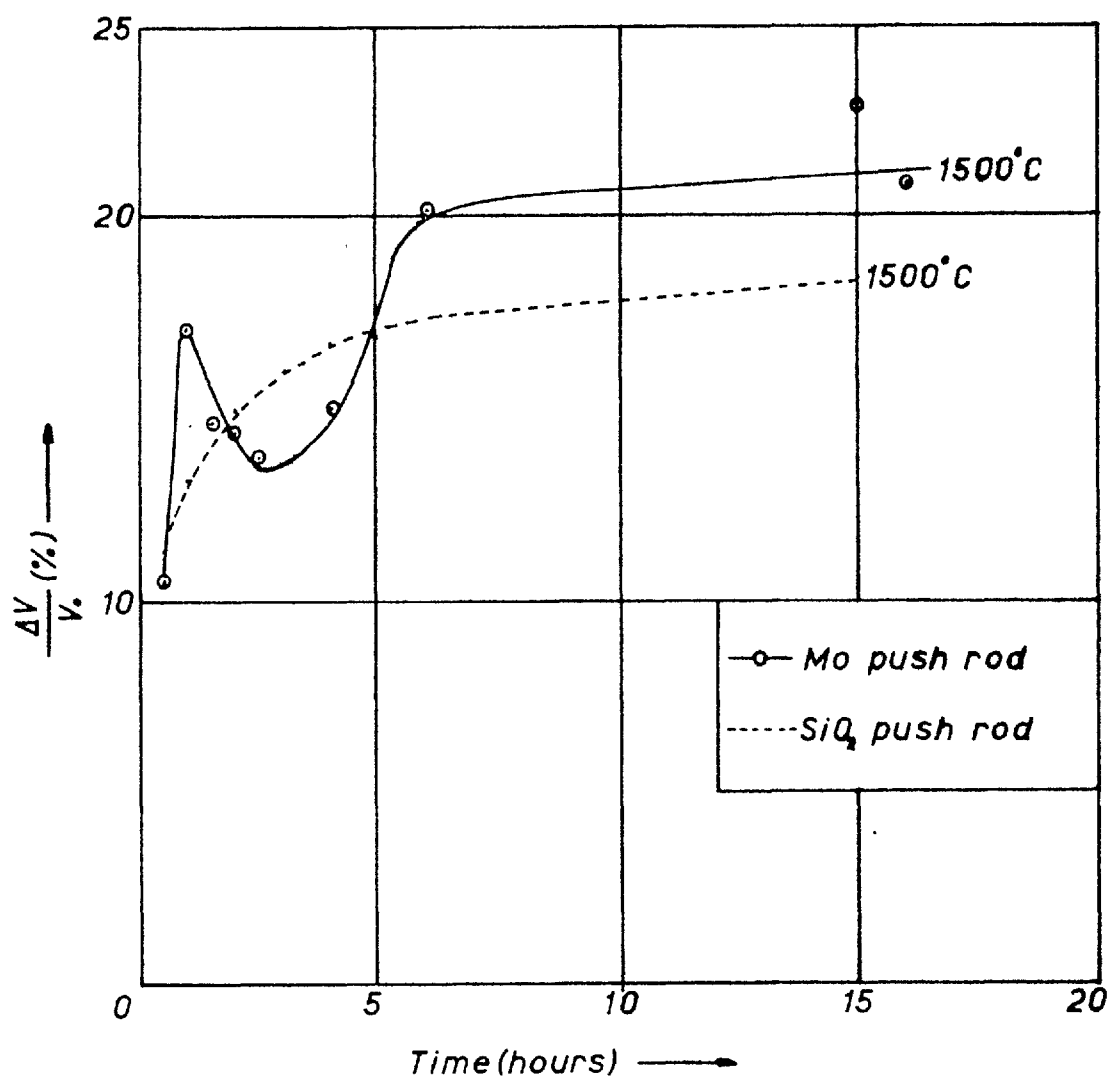


FIG. 7b Electronmicrograph of Plessy Alumina
ground for 1½ hrs. (X 2,000)

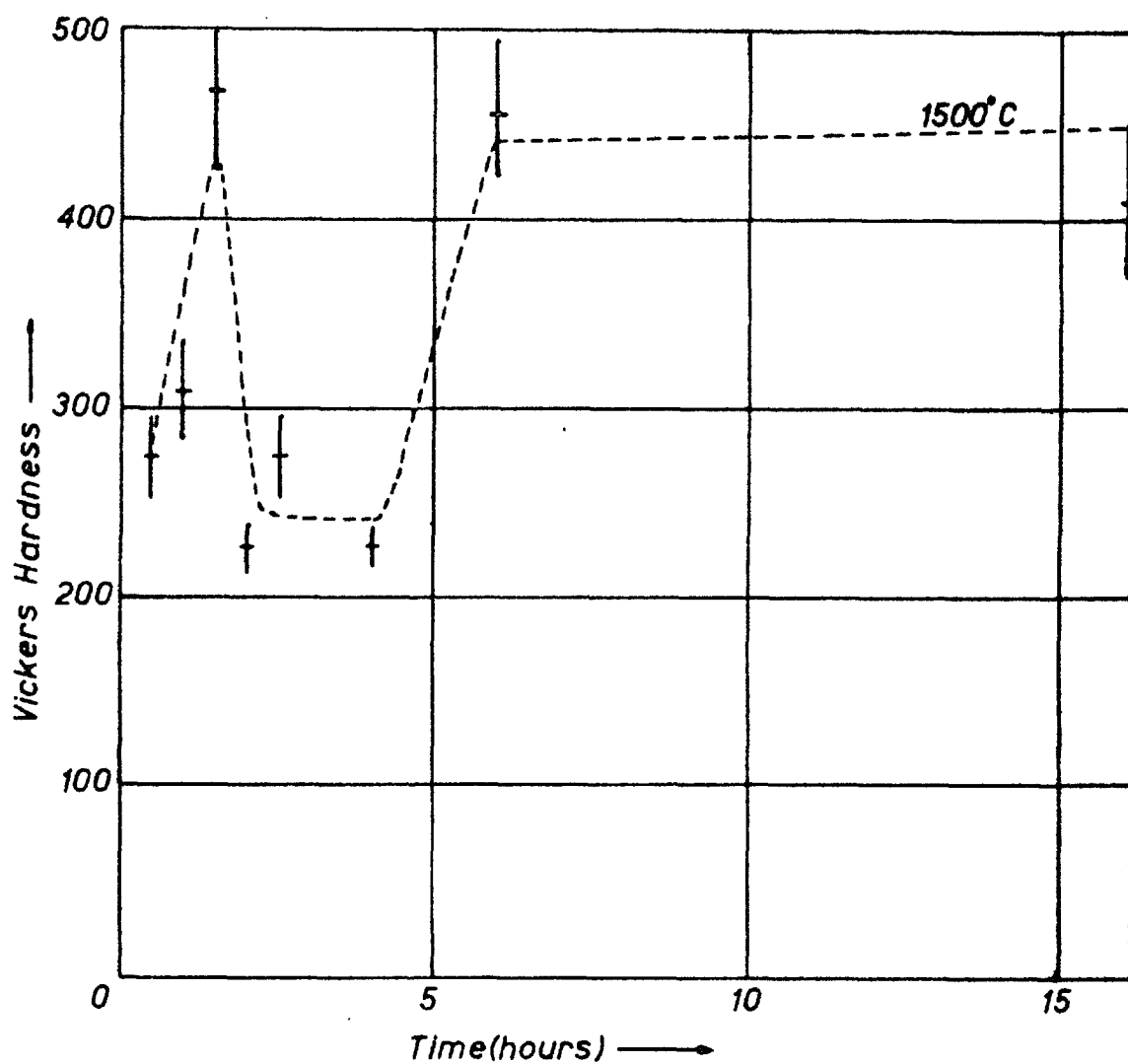
As has been explained beforehand the heating operations were standardized for each temperature, as the temperature gradient from the mouth of the furnace to the hot-zone changed with each temperature used. In the vacuum furnace a heating time of 10 minutes was used for all runs as previously stated, as the furnace was always started cold, and so subsequent heating could be controlled far more easily and quickly, thermal shock being almost negligible due to the use of metal parts throughout the furnace as opposed to the thermal shock susceptible impermeable furnace tubing, rails and boats used in the molybdenum furnace.

In preliminary work a molybdenum push-rod was used as the material was easily available and was still usable at the temperatures achieved in the furnace. It was thought at first that the oxidation of the rod while inserting or removing the specimen would have no effect on the sintering characteristics of the alumina. The results obtained were, however, to the contrary, as shown in Fig. 8, page 58. This gives a typical curve obtained for alumina at 1500°C , and similar curves were obtained at other temperatures. To explain this phenomenon, hardness tests were conducted on the specimens, x-ray analysis proving fruitless. The hardness values shown



'ANALAR' ALUMINA—SINTERED IN AIR

Fig. 8



HARDNESS MEASUREMENTS OF THE SPECIMENS SHOWN IN FIG. 8.

Fig. 9

in Fig. 9, page 59 follow the same general pattern as the volume change with time, which suggests a change in particle-particle bonding. The sharp increase in strength (indicated by the indentation hardness values) followed by a decrease in strength, and then a further increase to a constant value seems to indicate that material is transferred to the neck area and is then removed quickly, in a matter of half an hour. This "de-sintering" effect is tentatively attributed to the interaction of molybdenum oxide and alumina at the surface of the particles, producing non-stoichiometry in the surface and thus giving an enhanced defect structure, which increases ion mobility, and gives a sharp rise in the neck area, closing most of the open pores. On further heating the molybdenum oxide evaporates, due to a time dependent decrease in the concentration of the oxide in the surrounding atmosphere, and as the pores are now closed, it has to diffuse through the alumina as a gas, in so doing, forming more porosity which gives this de-sintering effect or bloating. The "plateau" in the diagram can be explained as the nulling of this de-sintering effect with the progressive sintering of the alumina. A comparison with alumina sintered at the same temperature, but using a non-oxidising push-rod (silica glass) given in the

same figure seems to confirm this idea. As the molybdenum push-rod masks the true sintering characteristics of alumina (and probably other oxides) it was decided to use silica glass rods for subsequent experiments as it had excellent thermal shock properties and did not vapourize.

Sensitivity of the Balance

The mercury balance was constructed after an idea by Eaton⁽³²⁾, as it was more sensitive and accurate than the model previously used in the laboratory⁽³³⁾.

The sensitivity of the apparatus was determined by measuring experimentally the density of a substance of known density, given in the following table:

TABLE II

	Reported Density (g/cc)	Volume Measured (cc)	Calculated Density (g/cc)	Percentage Error
Glass A	2.4926	0.0811	2.2158	11.1%
Glass B	2.4904	0.177	2.4393	2.1%
Glass C	2.4876	0.101	2.2387	10%

Great care was taken at all times to ensure that the mercury and the iron grab were clean with no powder adhering to cause discrepancies in weighing. The balance was kept in a constant temperature room to prevent undue temperature fluctuations during weighing which would affect the density of the mercury.

The specimen holder was first ly weighed in the mercury to find the upthrust on the holder alone. The specimen was then weighed in the mercury, after weighing in air on a balance weighing to 0.1 milligram. With care, the weight in mercury could be determined to 1 milligram, the third decimal place being used as a guide. The temperature of the mercury was recorded, and its density determined from tables. The volume of the specimen was determined as follows:

$$V = \frac{(W_A + W_{Hg})}{\rho_{Hg} \times W_A}$$

V = volume of the specimen, W_A = weight of the specimen in air, W_{Hg} = weight in mercury (or the upthrust), ρ_{Hg} = density of mercury.

Procedure for the Sintering of Alumina

In the literature it was observed that no single investigator had covered the whole range of sintering temperature

envisaged, i.e. from 1200°C - 2000°C , although different experiments had been conducted to cover different temperature ranges. It was thought desirable that this research should cover complete ranges of temperatures, as variations between investigators were unavoidable, especially in technique, mode of measurement of the sintering characteristics and most important of all, in the variation in the purity and in the particle characteristics which are evident when powders from different sources are used, as will be shown. The experimental procedure, as explained beforehand in the preliminary work, was adopted, and an investigation of the complete range of temperature undertaken.

Procedure for the Sintering of Alumina with Small Additions of Reactive Liquid

As the main work of other investigators⁽²⁸⁾ has been concerned with liquid additions greater than 10%, it was thought advisable to investigate the effect of small additives of liquid, from 1% - 10% by volume. This was done to establish whether such a small percentage would change the characteristics wholly to that of liquid-phase sintering or whether the reactive liquid would behave as an impurity causing lattice defects and, therefore, a greater ion mobility in the solid. Sodium silicate was chosen as this had a low melting point (1038°C) and its liquid

characteristics were known from previous corrosion work in this laboratory⁽³¹⁾.

The density of sodium silicate was calculated from the work of English and Turner⁽³⁵⁾, who give factors for SiO_2 and Na_2O to calculate the density from the composition as follows:

$$\frac{100}{D} = \frac{x^1}{d^1} + \frac{x^2}{d^2}$$

where D is the density of the glass, x^1 and x^2 are the percentages by weight of Na_2O and SiO_2 respectively, and d^1 and d^2 are the factors for the calculation for Na_2O and SiO_2 respectively (3.47 and 2.20).

$$\frac{100}{D} = \frac{50.8}{3.47} + \frac{49.2}{2.20}$$

$$D = 2.70 \text{ gm/cc for } \text{Na}_2\text{O} \cdot \text{SiO}_2$$

SECTION IV

A. Sources of Error

The technique employed for following the sintering process involved many different parameters, each having its own particular source of error. These sources are listed below under the different parameters (as headings), and an estimated error for some typical results are given in the tables.

Temperature Measurement:

The errors could be traced to three possible sources:

(1) The inherent error of the measuring device, which is large for the optical pyrometer, being about $\pm 10^{\circ}\text{C}$ in the range of temperature (1600°C - 1900°C) over which it was employed.

With a thermocouple, using a sensitive potentiometer, the error in measurement was only $\pm 2^{\circ}\text{C}$, this being at its worst at $1500 - 1600^{\circ}\text{C}$ due to volatilisation of the rhodium from the couple. This was minimised in the present work by frequently comparing the thermocouple used with a standard thermocouple.

(2) The variation of temperature during the course of the experiment due to a possible fluctuation of mains voltage.

For the molybdenum and vacuum furnaces this was reduced by using a "Regavolt" automatic voltage stabiliser, limiting the mains voltage fluctuation to within ± 1 volt.

The molybdenum and platinum furnaces were always brought up to a set temperature and left to stabilize for at least twelve hours, before the experiments were carried out. This could not be done with the vacuum furnace.

(3) The variation of position in the hot-zone would give a different temperature each run. This was also minimised by marking the push-rod and standardizing the boat-placing with the length of the rod to this mark. The boats used were always smaller than the actual hot-zone and placed in the middle of it

Time Measurement

The chief source of error in timing was always at the beginning and at the end of each run, when the specimen was being heated or cooling.

As the specimens were being pushed into the furnace and heated up, especially at the higher temperatures, then sintering in the transition stage between the hot zone and the colder regions of the furnace can take place, giving an additional shrinkage, difficult to evaluate.

A standard time of specimen heating was used at each

temperature to minimise the end effect, the time taken for sintering being taken from the instant the specimen was in the hot zone to the instant when it was removed from it. The least time used for any run was thirty minutes so as to minimise the end effect which is greatest for the lowest time used.

Error due to temperature and time

As the error at different times and temperatures are quite different, some arbitrary points have been taken and the error in change of specific volume due to an error in temperature and time estimated from the equation

$$\frac{\Delta V}{V_0} = k \frac{t^{2/5}}{T^{2/5}}$$

as put forward by Kingery and Berg⁽¹⁷⁾.

TABLE III

Average $\frac{\Delta V}{V_0}(\%)$	Furnace Temp. ($^{\circ}\text{C}$)	Temp Error ($^{\circ}\text{C}$)	Time (mins)	Time Error (mins)	Calculated Experimental Limits ($\frac{\Delta V}{V_0} \%$)
1.0	1235	± 5	30	± 3	± 0.04
3.62	1285	± 5	900	± 3	± 0.01
11.49	1500	± 5	30	± 3	± 0.46
19.68	1500	± 5	1140	± 3	± 0.05
36.6	1770	± 10	30	± 3	± 1.5
42.7	1770	± 10	720	± 3	± 0.15

Mercury Balance

The sensitivity of the balance is given in Table II , page 62 , which shows that the sensitivity increases with increasing specimen volume, and that the maximum error is - 2% of the volume measured.

The main source of error was found to be in the cleanliness of the mercury and in the constancy of its temperature.

- (1) The mercury was cleaned frequently, to ensure that no surface film was present which interfered with the upthrust

and with the density of the mercury. As the specimen was pushed underneath the mercury, any surface film would adhere to the specimen and give a false reading of the volume. Care was also taken to ensure that no air bubbles were trapped on the surface of the specimen, which would also interfere with the upthrust on the specimen.

(2) The temperature of the mercury affected its density, which was used in the calculation of specific volumes, and so, care was taken by using the mercury balance in a constant temperature room, and measuring its temperature at frequent intervals.

(3) The specimen holder was cleaned each time to remove surface films of powder adhering to it, and it was found necessary, especially with unfired specimens to measure the upthrust on it with each specimen. As the same volume of mercury was used each time, and the balance always brought to zero, the effect of the cross sectional area of the wire used was calculated but found to be negligible, but was kept small to give better sensitivity.

The specimen was balanced and the weight taken to three decimal places by use of a rider. The third place was used as a guide to establish the second place accurately.

Use of Specific Volume

As the sintering of the specimen was followed by a change in volume it was thought advisable to calculate the specific volume of the specimen so as to eliminate weight differences between each specimen, and to ensure that each specimen was approximately the same density for a fair comparison.

The shrinkage was then taken as the ratio of the change in volume (ΔV) to the initial specific volume (V_0) as this diminished slight differences due to different initial specific volumes and it gave a dimensionless number.

Error due to Losses in Weight

As the pellets made were initially of a friable nature, it was noticed that the weight of the specimen was less after firing than before firing, so that an error could be introduced due to the difference in weight of a pellet weighed in air and the actual weight as used in the calculation for the change in specific volume. On an average the weight loss was 1% for the pure alumina and 2% for the alumina with additions. A table of possible errors due to a loss in weight for the same arbitrary points as before is given below:

TABLE IV

Average $\frac{\Delta V}{V_0}$ (%)	Sintering Temp(°C)	Sintering Time (mins)	Loss in Weight (%)	Maximum Possible Error ($\frac{\Delta V}{V_0}$) %
1.0	1285	30	0.1	- 0.11
3.62	1285	900	0.1	- 0.13
11.49	1500	30	0.7	+ 0.14
19.68	1500	1140	0.9	+ 0.59
36.6	1770	30	0.25	+ 0.2
42.7	1770	720	0.27	+ 0.15

Minimising of Scatter

For a large part of the work, specimens were duplicated for each run to minimise scatter and possible errors due to a unique specimen, so that points on the curves are the mean of two values evaluated from the duplicated specimens. One experiment (Fig. 12 , page 80) was carried out using only one specimen at each temperature to verify that the curves obtained for different specimens were typical.

Specimens were fired for one time and one temperature only, and were not refired in subsequent runs. More points were evaluated for short times, i.e. between 30 minutes and

5 hours, as this was the range where the rate of shrinkage changed most. A representative curve was then drawn through the points.

B. RESULTS AND DISCUSSION

Sintering processes can be followed by observations from outside the materials, e.g. neck growth, shrinkage, strength and hardness, but sintering depends on internal factors such as the presence of vacancies and other point defects, the energy to create these, the jump frequency and the possible sinks to which vacancies can diffuse.

As the sintering process depends on several different variables, in assessing the overall process it is necessary to consider each factor in turn.

In the past, various authors have worked with one or two variables, to formulate the controlling mechanisms and the kinetics of sintering. Most work has been done on the mechanism of sintering, which is formulated from the effect of time on the process. Thus, Kuczynski⁽²⁾, Clark and White⁽⁴⁾, Kingery and Berg⁽³⁶⁾, Coble⁽²³⁾ among others have formulated theories of the mechanism by observing different phenomena associated with sintering. The kinetics of the system have also been worked out by these authors, by deriving diffusion coefficients from experimental observations.

The physical properties such as size and shape of

particles and presence of impurities are also factors which affect the sintering process, as has been shown by Coble⁽²⁷⁾, Cof⁽³⁰⁾, Gray⁽¹⁶⁾ and others, so that the present work endeavours to follow each parameter and to compare the results with previous work. An overall picture of the process can then be seen, as the techniques and materials used are the same throughout.

With liquid additions, previous workers such as Kingery and Narashiman⁽²⁸⁾, Lenel⁽³⁶⁾, Gurland and Norton⁽⁴⁰⁾ have used reactive liquids, such as metals and binary eutectics in a fairly large proportion. The present work is based on the addition of sodium silicate as the liquid-former, whose reactivity with alumina is known from work done on slag attack⁽³⁹⁾.

The work, therefore, is basically in two parts. First of all dealing with solid state sintering, and the effect of different parameters, and secondly, liquid-phase sintering.

1. Solid-State Sintering

The Effect of Time

Kingery and Berg⁽¹⁷⁾ formulated an equation giving the rate of approach of centres of particles as

$$\frac{\Delta L}{L} = \left[\frac{20 \gamma \delta^3 D_v}{3 a^3 k T} \right]^{2/5} t^{2/5}$$

ΔL = change of distance between centres of particle

L = original distance between particles

γ = surface tension

δ = ionic spacing

D_v = volume diffusion coefficient

a = radius of particles

k = Boltzmann constant

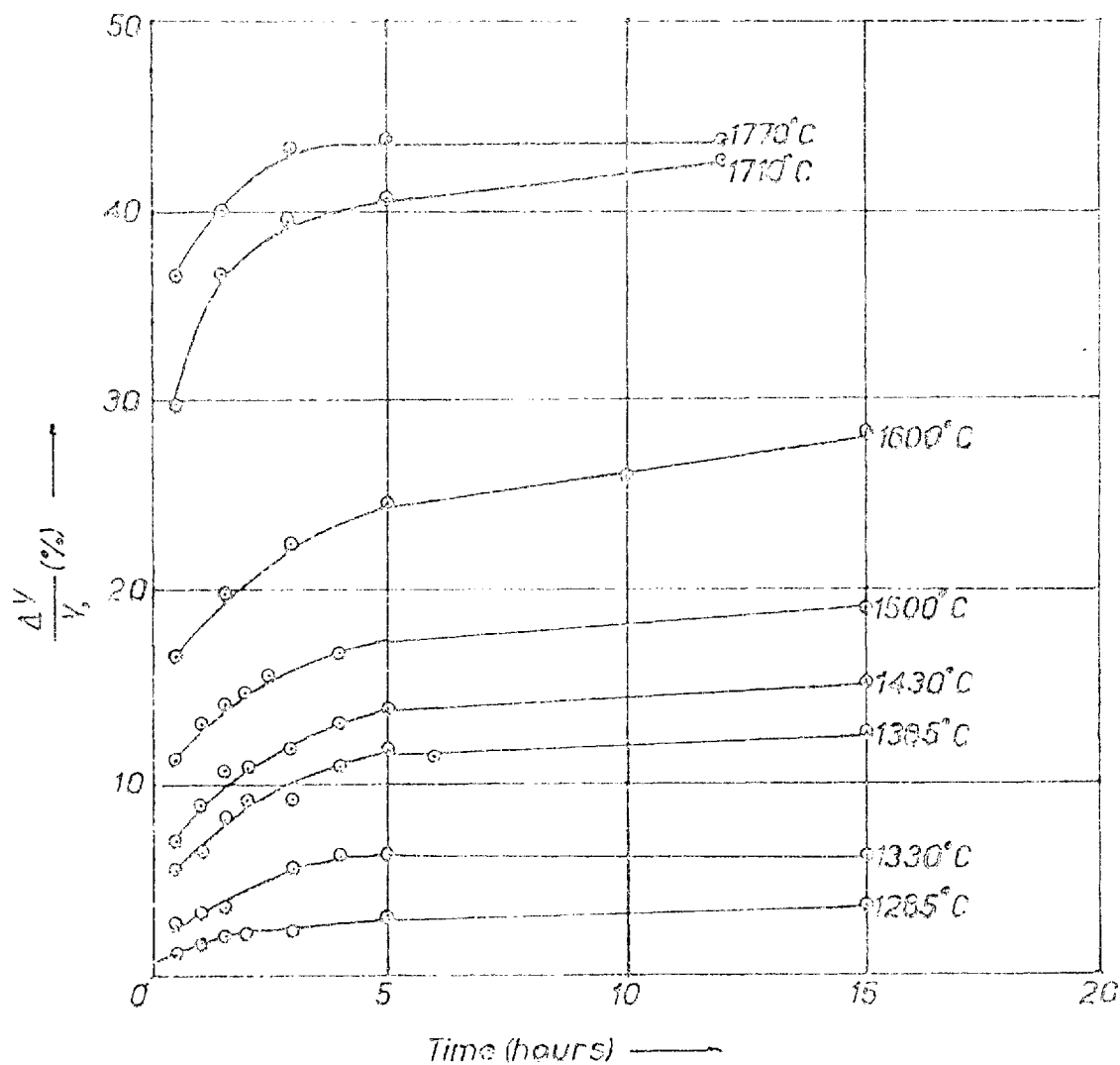
T = absolute temperature

t = time

The two fifth relationship was confirmed by the work of Coble⁽²³⁾ measuring the change in diameter of a powder compact. His work was carried out between 1150°C and 1350°C on alumina compacts, but at higher temperatures a decrease in the slope at longer times was observed, and concluded it was due to the ageing of the furnace elements. This has also been observed by Burke⁽⁴³⁾

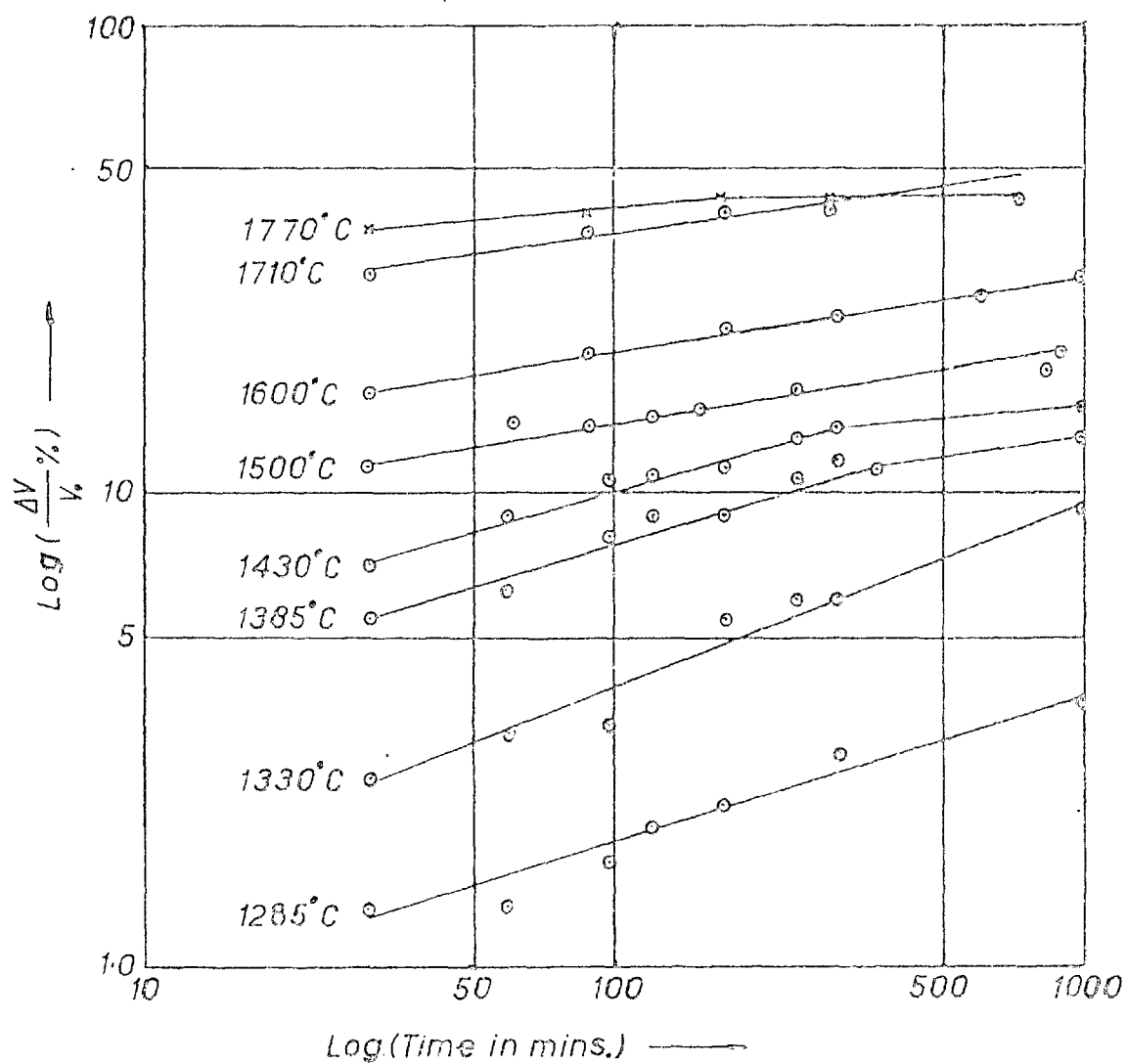
The present work, measuring volume shrinkage, as opposed to linear shrinkage, follows closely on Coble's work up to 1430°C , as shown in Fig. 11, page 79, as the relationship between linear shrinkage and volume shrinkage is merely one of dimension. It is interesting to note that the same decrease in slope is observed at longer times, at 1385°C and 1430°C also follows Coble's observations closely, but as ageing of the furnace did not occur, and frequent temperature checks were made, the same conclusions could not be drawn.

As the observations were carried out on a number of specimens, it was decided to use one specimen to diminish uncontrolled variables and to fire for various times at the same temperature, to confirm the results obtained with different specimens. This is shown in Fig. 12, page 80. The values obtained for the two temperatures were consistent with those obtained using different specimens, and verified the slopes. From these observations it is concluded that as the sintering progresses a change in the driving force of the system occurs, leading to a limiting density for each particular temperature. As the driving force for sintering is the concentration gradient of vacancies from the surface to the particle junction, then as sintering proceeds, this concentration gradient decreases as the temperature is low and the total concentration of vacancies



'ANALAR' ALUMINA —SINTERED IN AIR

Fig. 10



'ANALAR' ALUMINA

Fig.11

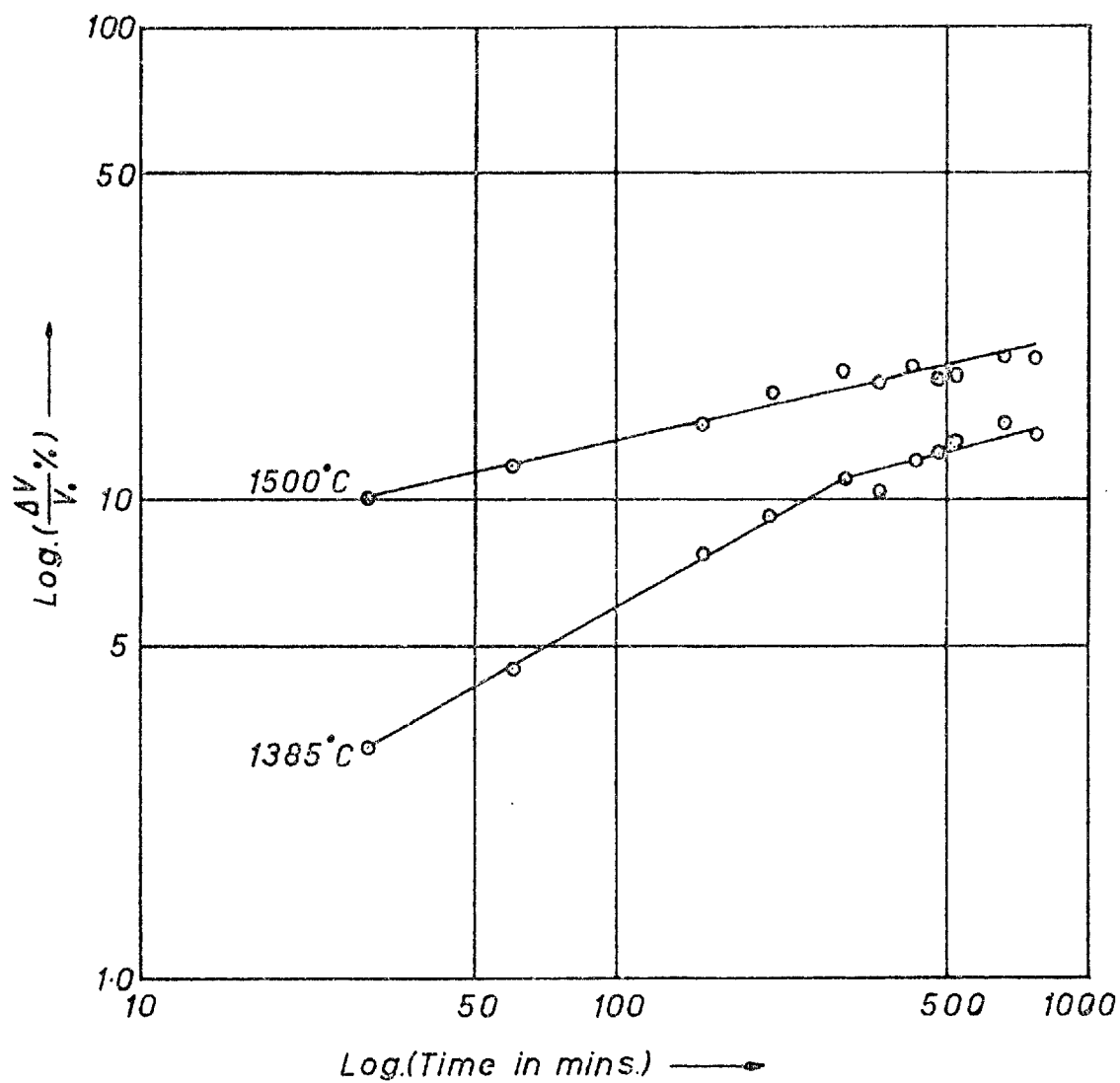


Fig. 12

is small⁽⁴¹⁾ and a relatively small change in vacancy concentration due to sintering reduces the driving force.

At temperatures of 1500°C and above, the slope of the line is approximately one fifth, which does not fit any of the current models of the sintering mechanism. At these temperatures, however, the exponential increase of vacancies in equilibrium reaches a point at which they interfere with one another and coalesce to form micropores; or perhaps, this formation reduces the concentration gradient from neck to surface, thus decreasing the driving force for sintering.

At temperatures of 1700°C and above, grain growth takes place (Fig. 13, pages 82,83), as has been observed by other workers, notably Cahoon and Christensen⁽⁴²⁾ and Burke⁽⁴³⁾. They showed that the grain boundary movement sweeps the pores in its path, but may leave isolated pores in the particles. The diffusion path of vacancies to the grain boundaries then becomes too long to be significant and the pores inside the particles then act as vacancy sinks. This is again shown in Fig. 13, with the much larger size of pores encountered, which may be as large as the original particle size. This effect becomes even more pronounced at temperatures approaching the melting point, and may even



Fig.13a. Thin section of Alumina sintered at 1600°C. for 10hrs. in air (x400)

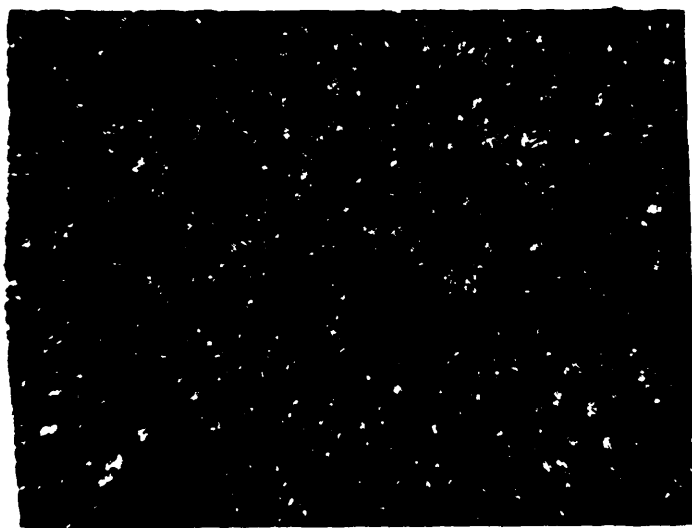


FIG.13b. Thin section of Alumina sintered at 1770°C for 12 hrs. in air (X 400)

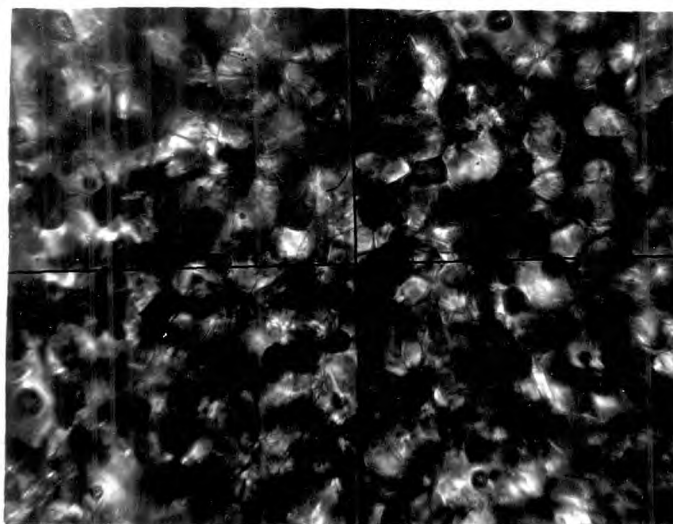


Fig.13c. Thin section of Alumina sintered at 1950°C. for 30 mins. in vacuo (x400)

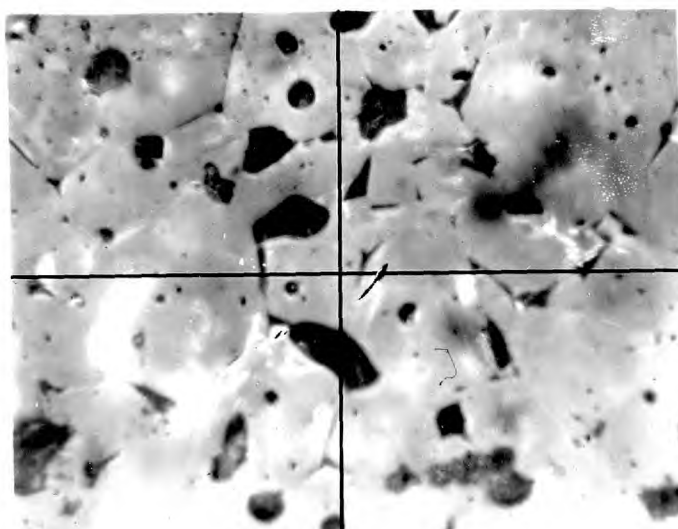


Fig.13d. Polished section of Alumina sintered at 1950°C. for 1hr. in vacuo (x400)

give a 'de-sintering' effect, as shown in Fig. 10, page 78 .

Effect of Temperature

The effect of temperature is derived from the equation:

$$D = D_0 e^{-E/RT}$$

where D = Diffusion coefficient

D_0 = constant

E = Activation Energy

R = Gas constant

T = Absolute temperature

It can be seen that to evaluate accurate determinations of activation energies, E , that the Diffusion coefficient for the process must be known, and in order to do this the diffusing species must also be known. For self-diffusion this can quite easily be assessed, but for a complicated process like sintering it is extremely difficult to know the exact diffusing species, especially for the complicated systems, e.g. Al_2O_3 .

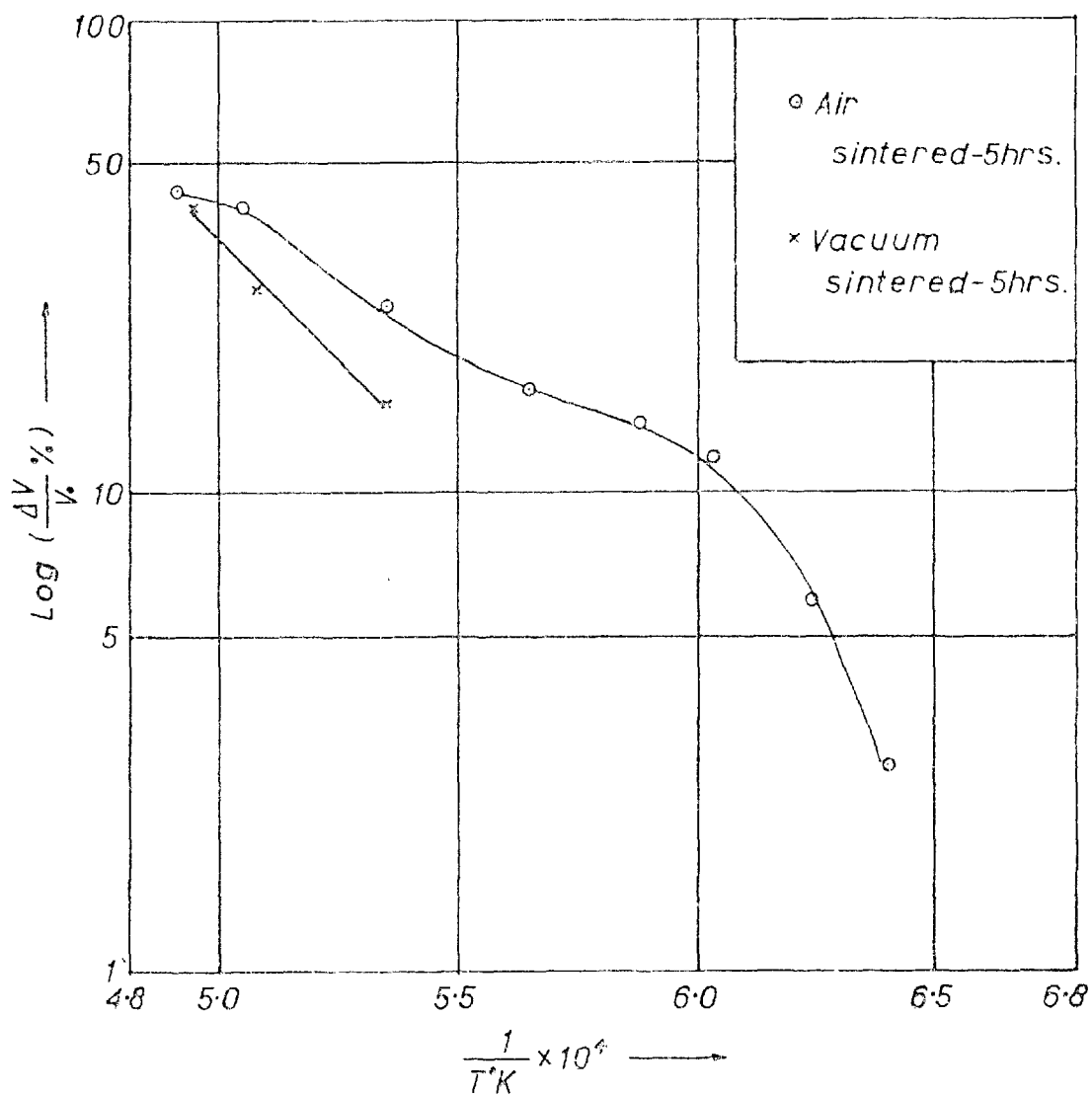
In the past various investigators^(2,4,17,23) have formulated expressions relating the diffusion coefficient for sintering with experimental observations, e.g. shrinking or neck growth. The variation in results obtained for activation

energies were from 87 k.cals/mole in Clark and White's work to 165 k.cals/mole for Kuczynski's determination. As both these investigators were working in different temperature ranges, i.e. Clark and White from 1200°C to 1600°C, Kuczynski from 1700°C to 1900°C, the difference in values obtained could indicate a difference in the mechanism of the process at low temperatures and at high temperatures.

The present work does not claim to give absolute values of activation energy, and only a qualitative picture is given to confirm the previous section of the work.

In Fig. 14, page 86 the change in slope at approximately 1450°C is in agreement with the view that a change in overall mechanism takes place, with the exponential rise in the equilibrium concentration of vacancies decreasing the overall rate of shrinkage. This is analogous to the observations of Austerman⁽⁴⁴⁾ conducting work on the diffusion of beryllium through beryllium oxide, who concluded that the effect was due to the presence of impurities affecting the number of defects present in the lattice at low temperatures.

As can be seen at a later stage in the effect of 1% additives, page 908, this is not at the same temperature, but at 1265°C, which indicates that, additives, or impurity additions decreases the temperature at which the "anchoring" of defects



'ANALAR' ALUMINA

Fig.14

is diminished , and ionic mobility is increased.

At temperatures above 1700°C the interference of grain-growth, as described in the previous section, prevents any further sintering from taking place. The change in slope of this type was observed by Clark and White⁽⁴⁾ and attributed to the change in the yield stress with rise in temperature, in accordance with their plastic flow mechanism.

Effect of Prefiring on Sintering

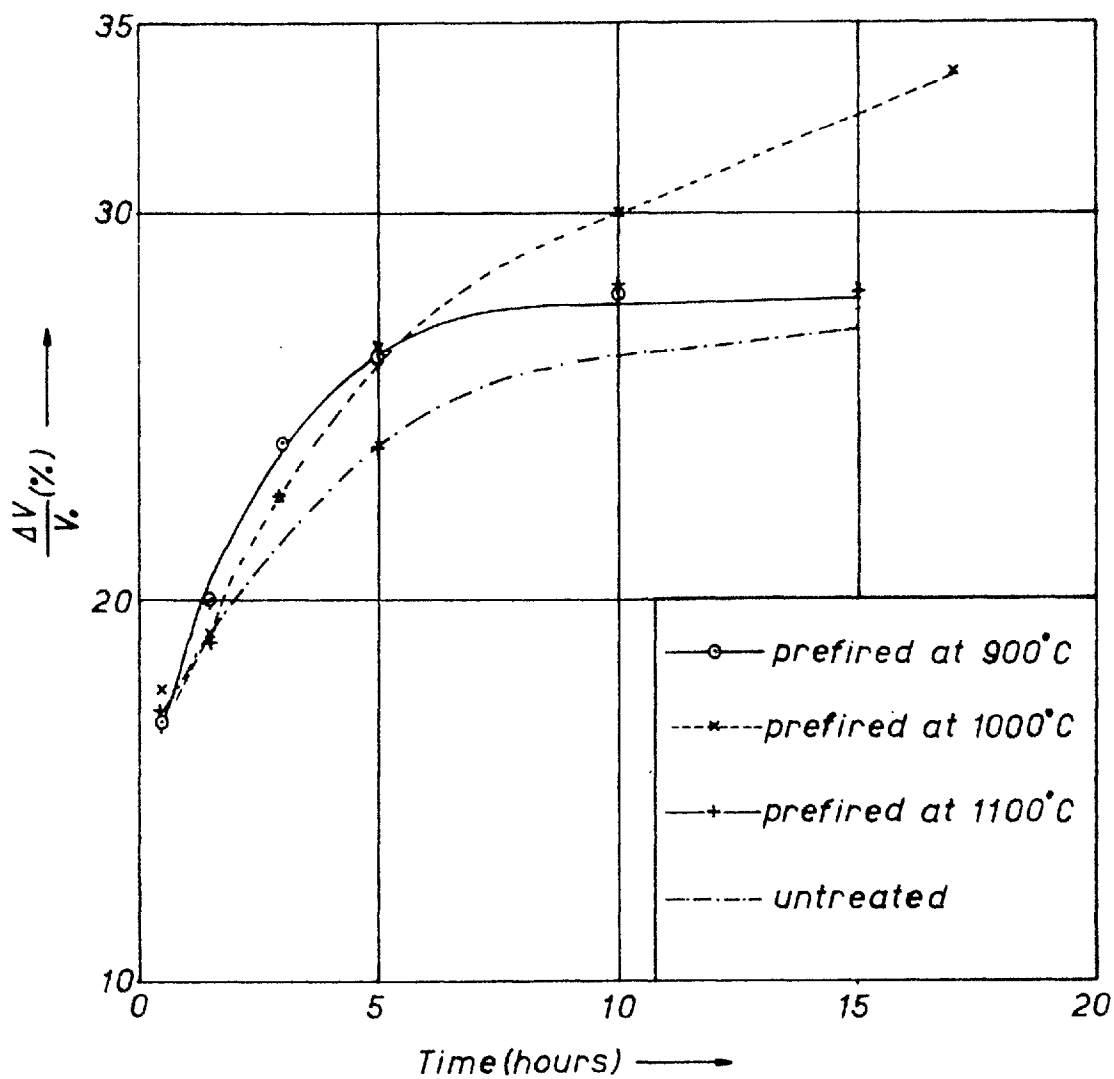
Although the effect of prefiring has been known empirically for a number of years, no theory or hypothesis seems to have been formulated, although it has been observed⁽⁴⁵⁾. The present work was carried out to clarify the situation as far as possible. Three prefiring temperatures were chosen, 900°C , 1000°C and 1100°C . Specimens were prefired at these temperatures for 1 hour and then sintered at 1600°C for various times. Longer periods of prefiring had little or no effect on the shrinkage after the treatment.

Shrinkage due to prefiring was also carried out, and for 900°C and 1000°C this was negligible. For 1100°C , however there was a slight increase in density, but in order to make a fair comparison, only the shrinkage after sintering was taken into account. The plot of the curves is shown in.

Fig. 15, page 89 .

The increase in shrinkage with prefiring up to 1000°C indicates that the driving force for the process is increased. It was observed that the pellets were more handlable after prefiring showing that some adhesion of the particles had taken place. This is attributed to surface diffusion taking place, even at temperatures below that at which lattice mobility occurs. This is in accordance with the work of Huttig⁽³⁷⁾, which states that surface diffusion occurs at a much lower temperature. This would not cause shrinkage of the material, but would help in the formation of the necks. The "surface" through which diffusion takes place would be a layer of material, the thickness of this layer increasing with temperature, so that at higher temperatures there would be larger necks formed. The establishment of the necks during prefiring would facilitate the subsequent volume diffusion and shrinkage.

The drop in shrinkage from the optimum temperature of prefiring (1000°C) to that at 1100°C is caused by the onset of lattice mobility which starts at approximately 1100°C . If shrinkage were calculated from the volume of specimens before prefiring, then the shrinkage values for pellets prefired at 1000°C and 1100°C would be approximately the same at the same sintering temperature.



The effect of pre-firing on the sintering of Alumina at 1600°C.

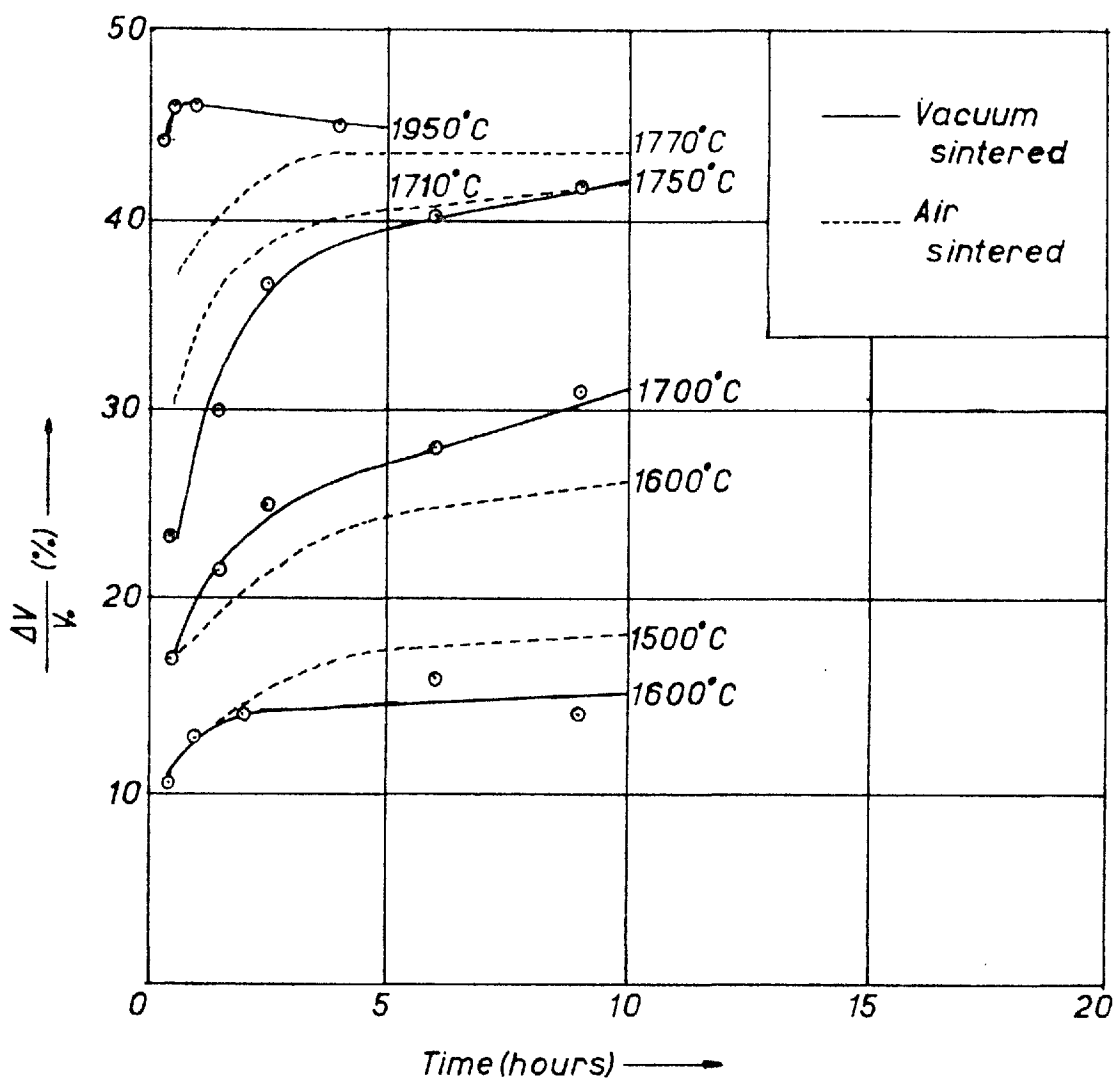
Fig.15

It seems clear that at temperatures below the Tammann temperature, surface diffusion alone is present, and that above this temperature volume diffusion is also operative. The effect of surface diffusion is important in that it establishes the formation of the necks for the subsequent volume diffusion, and it is feasible that this effect will occur whilst the pellet or compact is being heated up to the sintering temperature. Although it cannot be proved, it also seems evident that the surface diffusion does still continue at high sintering temperatures, but is masked completely by the faster volume diffusion mechanism, due to lattice mobility.

Effect of Vacuum on Sintering

A comparison of the sintering process in air and in vacuum could only be followed between 1600°C and 1800°C due to the temperature ceiling of the molybdenum furnace and the lower limit of the optical pyrometer used on the vacuum furnace. A comparison of the curves is shown in Fig. 16, page 91, which gives lower values of shrinkage for vacuum sintering than for air sintering at comparable temperatures. The effect of temperature is shown in Fig. 14, page 86.

The difference in the degree of sintering achieved in the furnaces is due to the difference of the surrounding media. Thus in the vacuum furnace the very low pressures encountered



'ANALAR' ALUMINA

Fig. 16

(10^{-5} mm Hg) and the high temperatures used cause evaporation of the surface layers, as occurs in the technique of thermal etching, where the grain boundaries, or in this case, the particle-particle junction is in a high state of disorder, and therefore, the bonding is weaker. Material is then vapourized from the particle junctions, thus lessening the defect nature of the surface, and lowering its surface energy. A loss in weight of the specimen was also observed depending on the temperature of sintering.

TABLE V

Sintering Temp. °C	Sintering Time hrs.	Original Wt. (gms)	Loss in Wt. (gms)
1950	4	.9492	.0604
1950	$\frac{1}{2}$	.9548	.0218
1700	4	.9671	.0115
1700	$\frac{1}{2}$	.9494	.0079
1600	6	.9032	.0100
1600	$\frac{1}{2}$	.9952	.0105

The loss in weight was also due in part to the friable nature of the unfired specimen, at the most being 0.006 gr.

A comparative test was carried out at 1800°C between

a piece of single crystal sapphire and a specimen previously fired to 1900°C with 10% porosity. The results in the loss in weight are given below:

TABLE VI

Both specimens heated at 1800°C for 6 hours in vacuo.

Specimen	Original Weight	Loss in Weight
Sapphire	.99465 gm	.00085 gm
Sintered Alumina (10% porosity)	.91355 gm	.0033 gm

Both specimens were of comparable surface area, so that the loss in weight verifies the results shown in Table V, and the hypothesis put forward.

Cabrera⁽³⁸⁾ considered the ratio of the excess concentration of vacancies at the concave surface of a neck to the concentration at a point in a plane surface to be as follows:

$$\frac{\Delta N}{N} \approx \frac{\gamma \delta^2}{k T r}$$

where ΔN = excess concentration of vacancies

N = concentration of vacancies at a plane surface

γ = surface energy

k = Boltzmann constant

r = particle radius

δ = ionic spacing

T = absolute temperature.

Then, as the excess concentration of vacancies is decreased by evaporation from the disordered layer in vacuo, the surface energy of the particle is decreased, giving a diminished driving force for sintering.

Effect of Particle Size

When a purer form of alumina was introduced (Plessey alumina) to check results found with analytical reagent quality material, there was inevitably a change of particle shape and size distribution. An effort was made to approximate the size distribution of the Plessey alumina to that of the analytic reagent material, but this was found to be practically impossible because of the nature of the shape of the initial powder. The best approximation is shown in Fig. 17, page 56, with the particle size distribution in Fig. 6, page 55.

The compacted density of the Plessey alumina was approximately 1 gm/cc, whilst that of the "Analar" alumina was approximately 1.8 gm/cc. The difference in the

sintering characteristics was inevitably tied up with this difference in size distribution, and a representative curve is shown in Fig. 17, page 96 to mark this difference.

This is due to the higher surface area of the Plessey alumina powder, which would give a higher surface energy, which increases the driving force for sintering. This is in agreement with Coble⁽²⁷⁾ who showed that the neck growth was related to the particle radius by the equation

$$\left(\frac{x}{R}\right)^5 = \frac{1}{R^3} (G) t$$

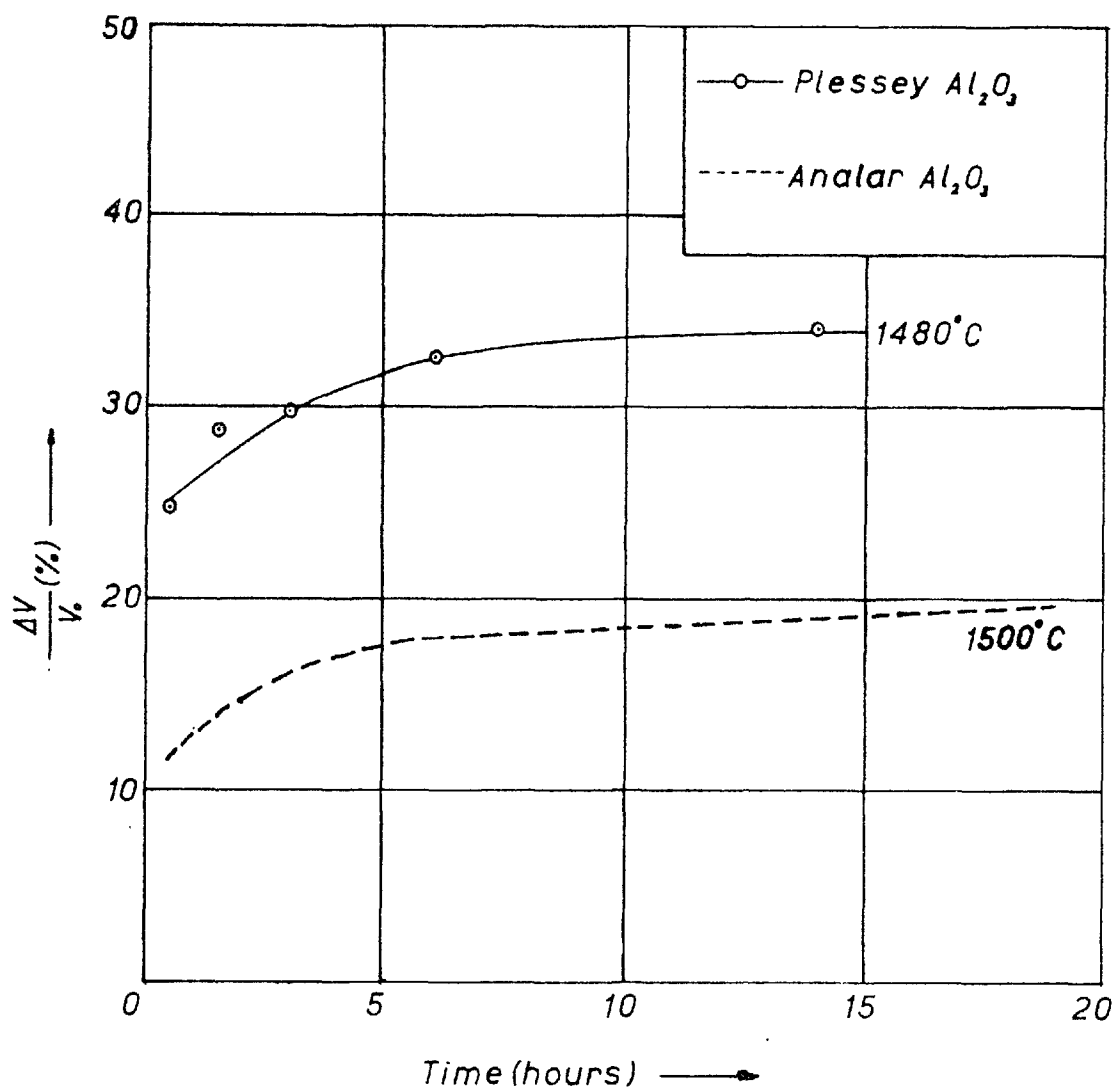
where x = neck radius

R = particle radius

G = constant

t = time for sintering.

This indicates that small particles will sinter more than larger particles for a given time, and at particle radii of approximately 1 micron, the effect of a small variation in particle radius magnifies the difference in neck growth and shrinkage.



The effect of Particle Size on Sintering

Fig.17

2. Liquid-Phase Sintering

Previous workers^(28,36,40) have dealt extensively with liquid additions of 10% and greater and have shown that diffusion through the liquid-phase plays a very important part in the sintering process. In the present work three additions of 1%, 5% and 10% of liquid by volume were used to compare and contrast this behaviour with those observed for greater liquid additions.

Lenel⁽³⁶⁾ has stated that there are three stages in liquid-phase sintering:

- (a) rearrangement of the solid particles in the liquid to give densification;
- (b) solution of the solid in the liquid from the particle junction and reprecipitation on the surface of the particles;
- (c) solid state sintering due to the formation of a solid skeleton.

He also states that an appreciable amount of liquid must be present to allow these three steps to occur and the liquid must wet the solid and be reactive.

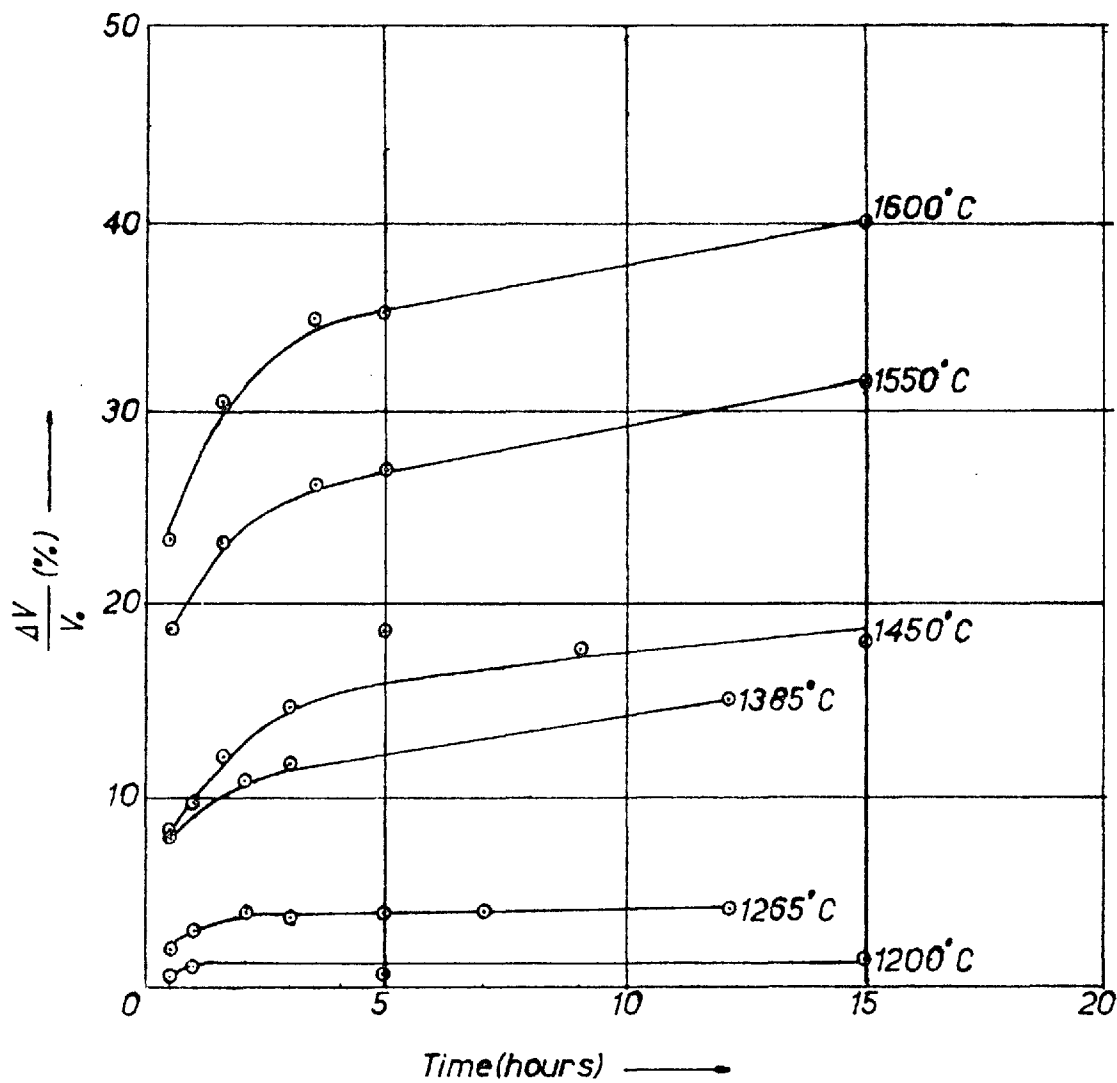
The present work shows that the effect of smaller additions of liquid on the sintering process is quite considerable,

but that 1% addition does not give liquid-phase sintering.

Price, Smithells and Williams⁽⁴⁹⁾ have shown also that there is an overall grain growth of the solid particles, also indicative of liquid-phase sintering. This is caused by the faster dissolution of smaller particles with consequent precipitation on the larger particles so that a structure of equal particle size and high density is formed.

Addition of 1% by Volume of Sodium Silicate

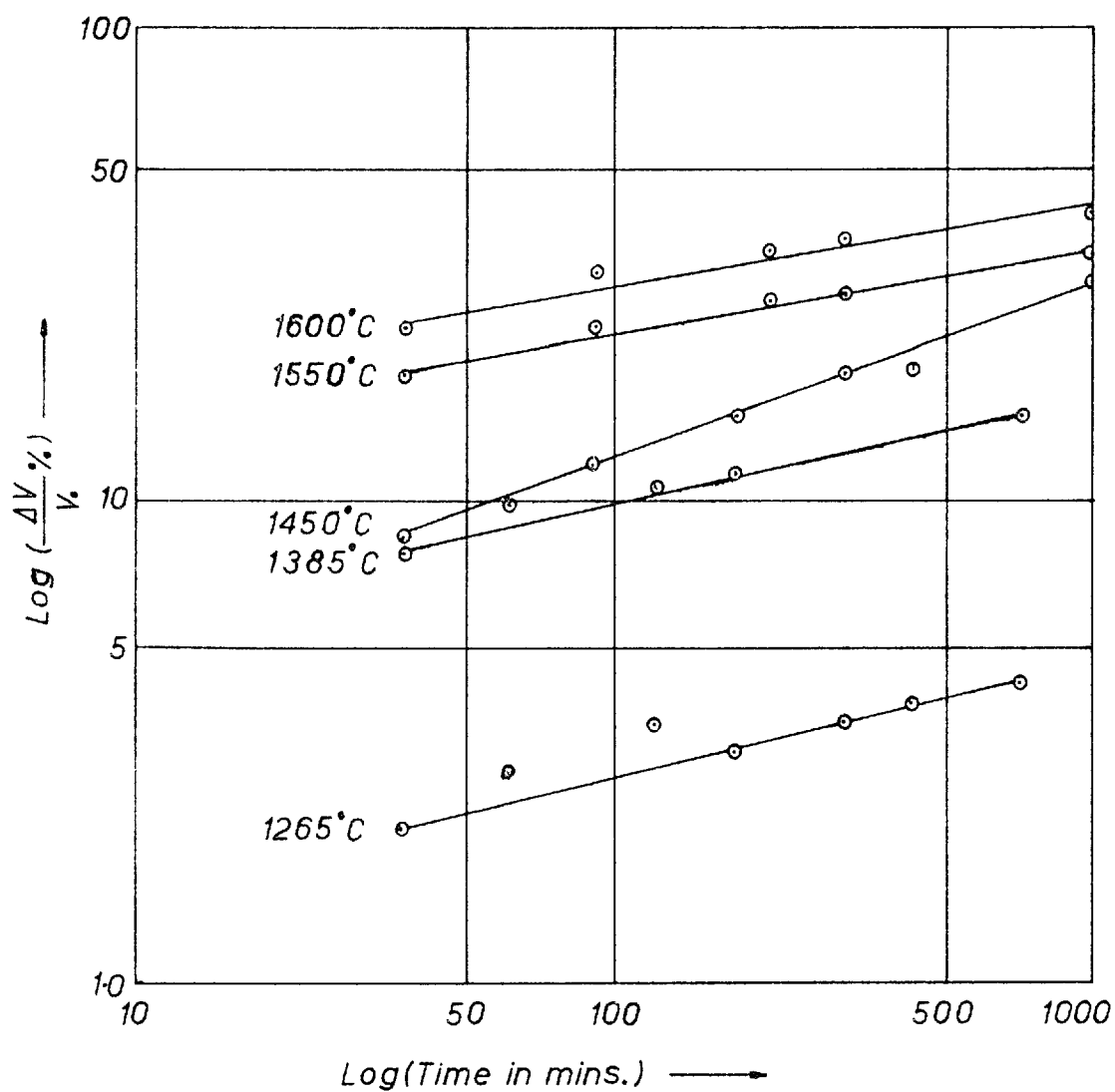
From the results shown in Fig. 18, page 99 , and Fig. 19, page 100 , it is evident that 1% addition of sodium silicate to alumina does not give liquid-phase sintering of the kind described by Lenel. The slopes of the lines in Fig. 19 give a one fifth power relationship between shrinkage and time, as has been described in the work carried out on pure alumina. It can be observed, however, that the one fifth relationship extends below a temperature of 1430°C and indicates that unlike pure alumina this behaviour is consistent with the view that defects are formed in the structure at these lower temperatures giving two opposing mechanisms of shrinkage and vacancy interference or micropore formation. There seemed to be no limiting density observed, presumably because of the constant



'ANALAR' ALUMINA

with 1% Sodium Silicate addition

Fig.18



'ANALAR' ALUMINA
with 1% Sodium Silicate addition

Fig.19

interaction of the sodium silicate as an impurity. The enhanced sintering which is observed on comparison of Fig. 18, with Fig. 10, page 78, also confirms the formation of defects and increased ion mobility. This is tentatively put forward as the reaction of sodium oxide and alumina to give β -alumina $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$.

The effect of additions of impurity atoms has been shown in analogous systems such as creep and plastic deformation⁽⁴⁶⁾ to increase the mobility of vacancies by interaction with the dislocations present. Other investigators^(47,48) have observed the effect of additions on the defect structures and subsequent diffusion processes.

Additions are also made which react chemically with the solid to give a difference in sintering properties, e.g. in all additions of magnesia are made to alumina to give a translucent body of almost theoretical density, because of the small amounts of eutectic formed between the magnesia and alumina which inhibits grain growth and allows the densification to proceed to the theoretical value.

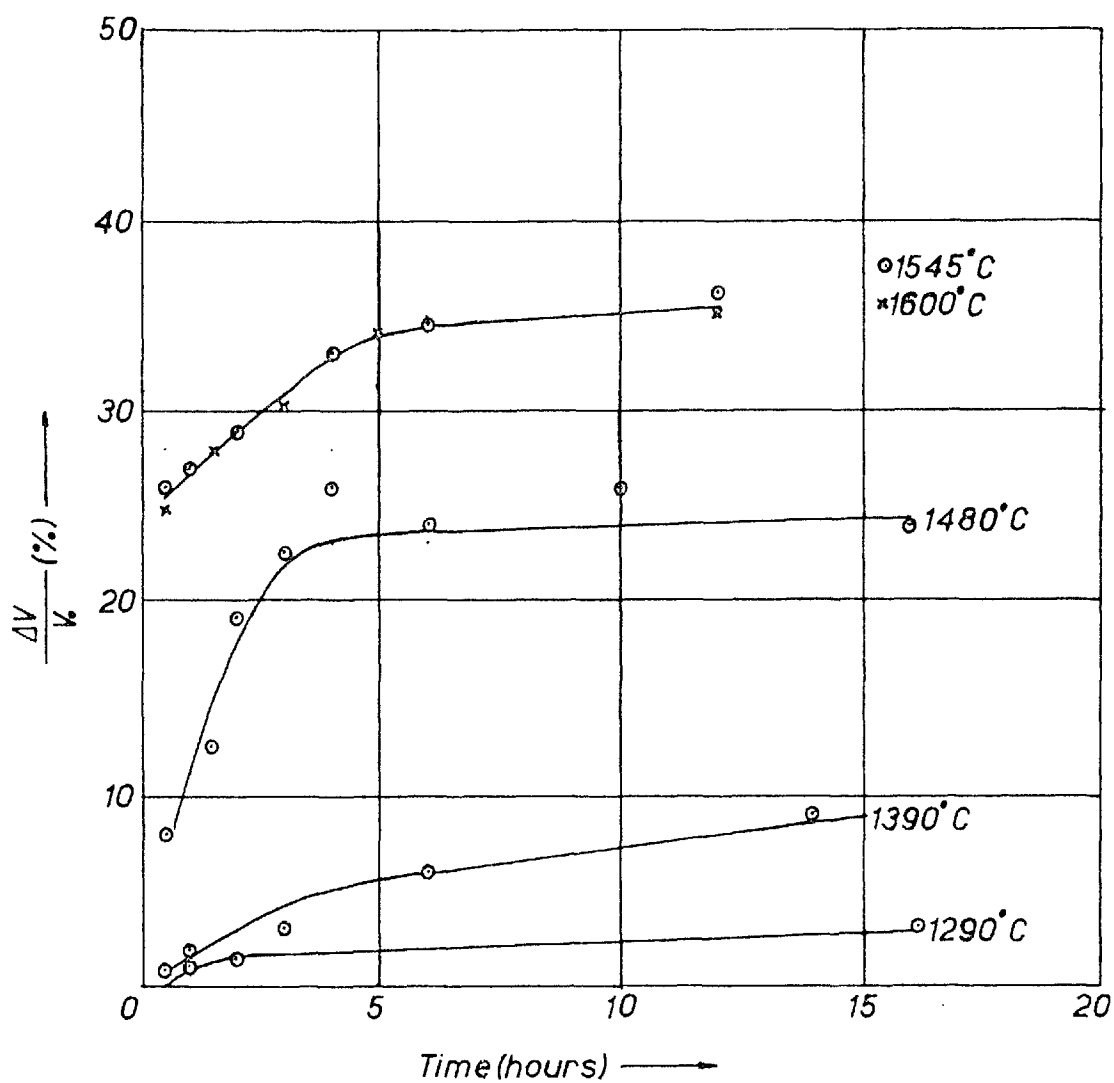
The enhanced sintering as seen in the inverse temperature plot, Fig. 24, page 108, indicates an activation energy approximately the same as for the sintering of pure

alumina. The temperature at which the change of mechanism occurs is lower than that for pure alumina, as has been indicated before. This confirms the idea that the addition of 1% sodium silicate depresses the temperature at which ion mobility is enhanced by the freeing of vacancies from this anchored position.

Addition of 5% by Volume of Sodium Silicate

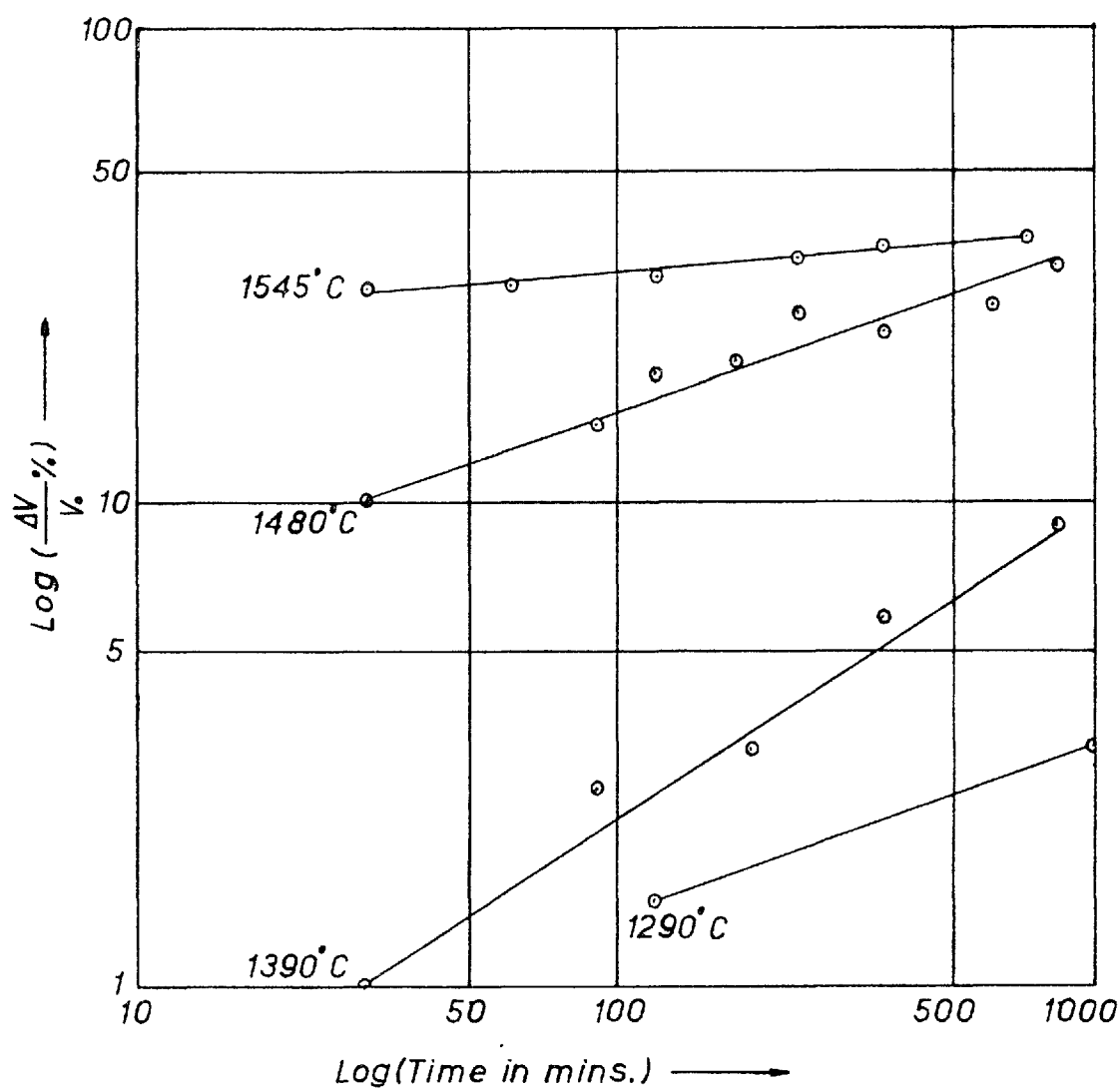
The results given in Fig. 20, page 103, and in Fig. 24, page 104 show that the addition of 5% sodium silicate gives evidence of liquid-phase sintering. The slope of one third for the log-log plots are in agreement with Lenel's second criterion of liquid-phase sintering and of Kingery and Narasimhan's⁽²⁸⁾ quantitative formulation of the process of solution at the junctions of particles with reprecipitation on the surface away from the line of contact.

This evidence of liquid-phase sintering with 5% by volume addition indicates that the amount of liquid governing the diffusion to form necks is relatively small and that it is the amount of liquid necessary to form lenses between the particles, that is the controlling factor in the second stage. Greater amounts of liquid will only affect the initial rearranging of the particles and not the second stage,



'ANALAR' ALUMINA
with 5% Sodium Silicate addition

Fig. 20.



'ANALAR' ALUMINA
with 5% Sodium Silicate addition

Fig. 21.

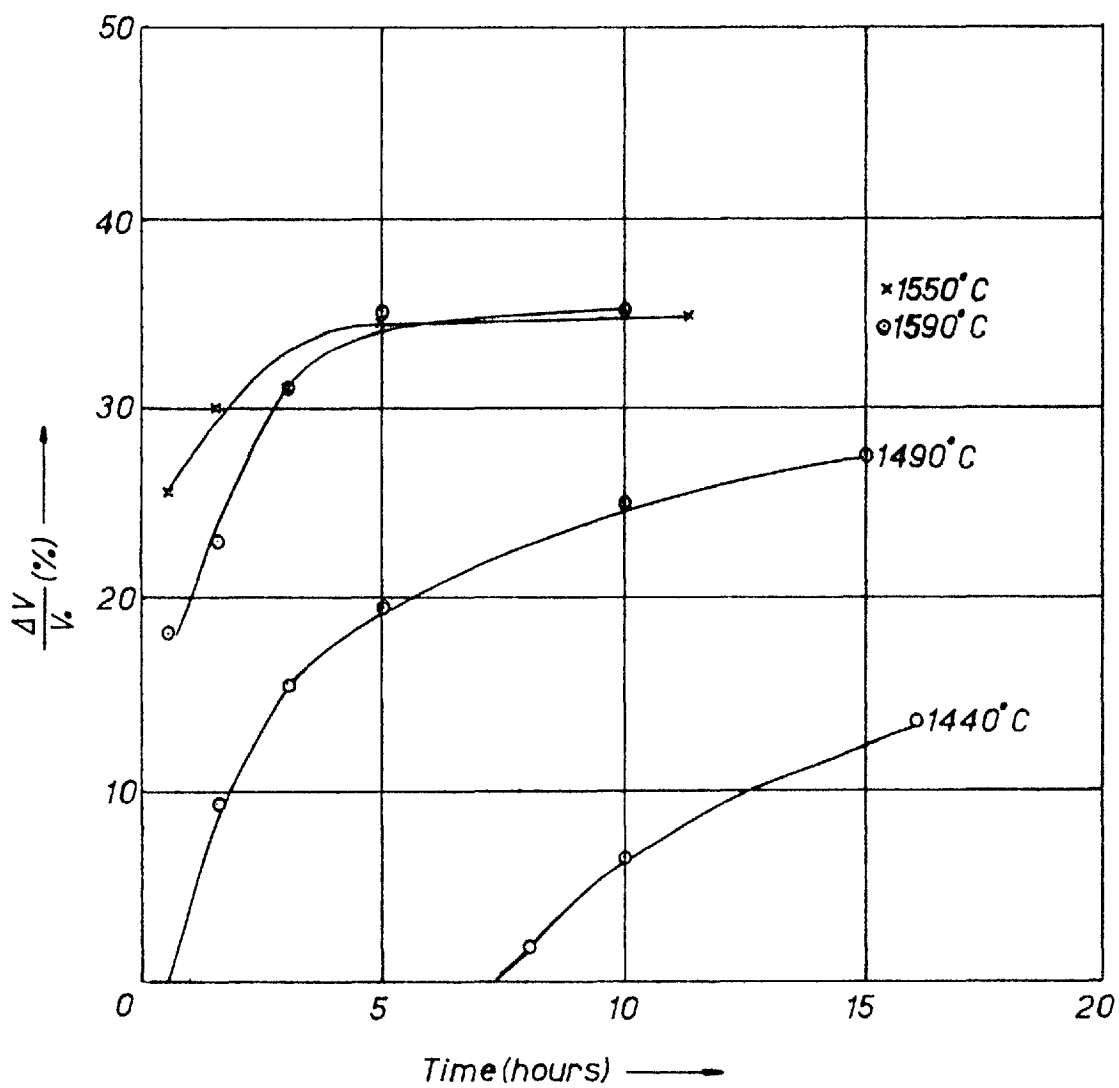
where any excess becomes superfluous.

At higher temperatures ($> 1500^{\circ}\text{C}$) the first two processes are completed before shrinkage measurements are taken (30 minutes). This is due to the higher mobility of the liquid and the higher solution rate of the solid in the liquid. The slopes observed, being one fifth, are then for the third stage of sintering, that of sintering of a solid skeleton of alumina. The liquid, saturated with alumina, takes no further part in the sintering process, and, in fact, retards the shrinkage by exerting a force on the surrounding skeleton due to the liquid tending to be compressed.

Addition of 10% by Volume of Sodium Silicate

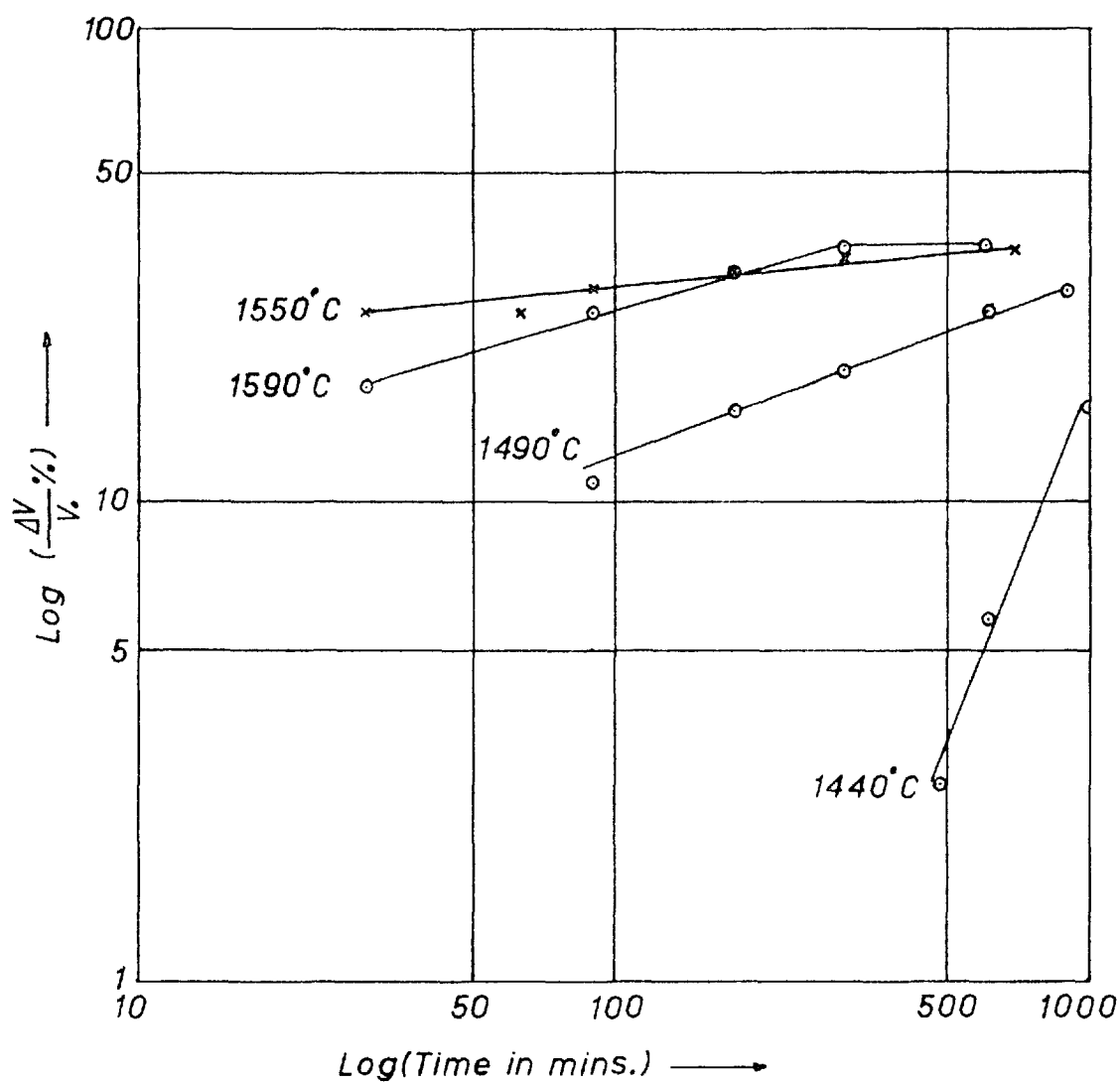
As in the case of the 5% addition the results in Fig. 22, page 106 and Fig. 23, page 107 show that liquid-phase sintering is taking place and a comparison of the two curves in Fig. 24 shows that there is only a relatively small difference between the sintering rates of alumina plus the two additions, which supports the idea that only a critical amount of liquid is necessary to form the lenses through which diffusion takes place.

On comparing Figs. 22 and 20 it can be seen that the temperature at which sintering begins to take place rises



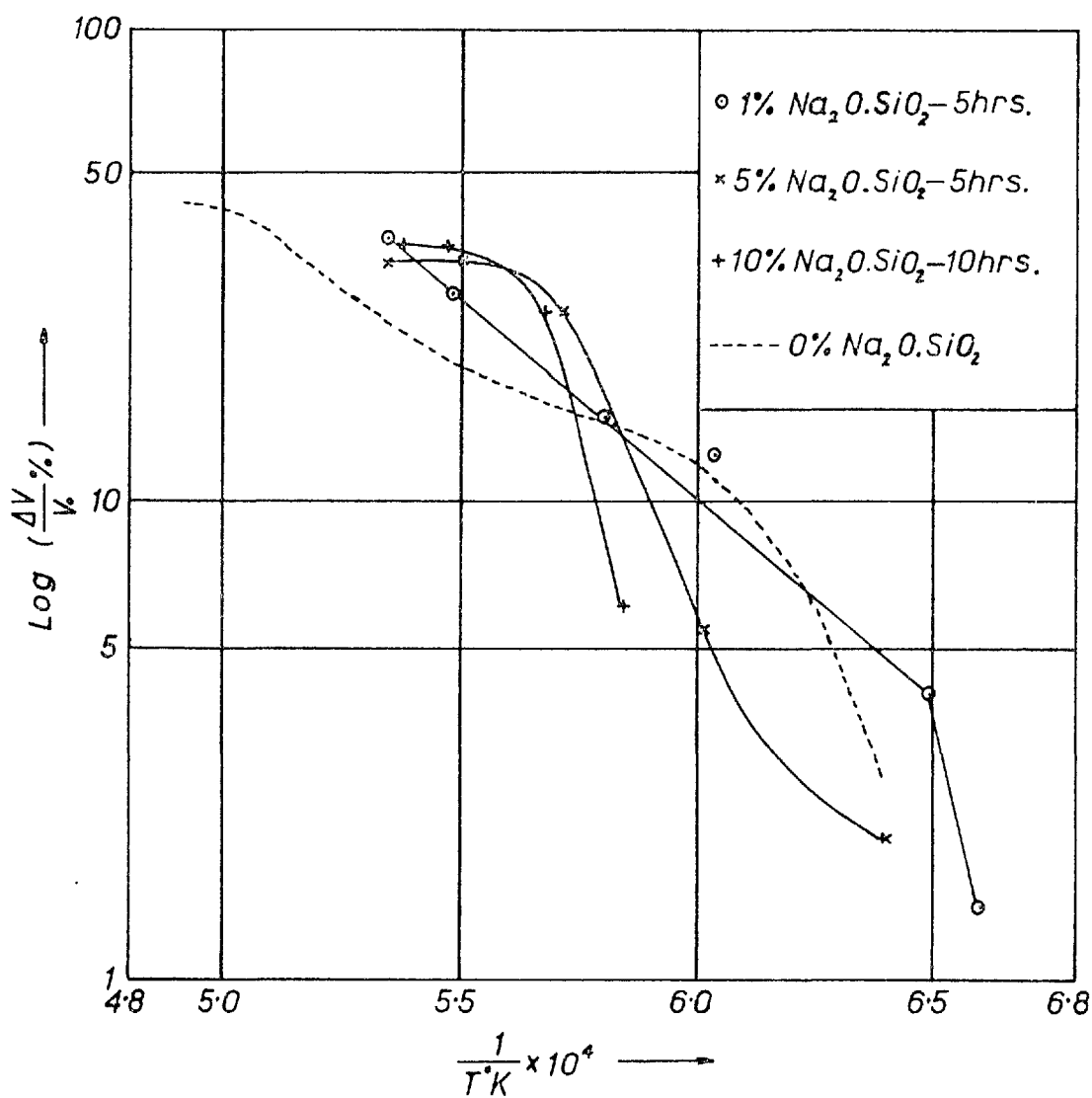
'ANALAR' ALUMINA
with 10% Sodium Silicate
addition

Fig. 22.



'ANALAR' ALUMINA
with 10% Sodium Silicate addition

Fig.23.



The Temperature effect of Sodium Silicate additions

Fig. 24.

with increased silicate content. This was thought to be due to the presence of water (Table VII , page 110) in the sodium silicate, being driven off as the temperatures is raised causing bloating of the specimens. Specimens fired below these temperatures showed an expansion after firing of 2-3% which gradually decreased with time and increased temperature. A secondary experiment was carried out using two pellets, one of the 10% addition used in the experiments undertaken, and a similar pellet with an additional (10%) amount of water. The first pellet expanded after firing to 1400°C for 30 minutes by 0.6%, whilst the second pellet expanded by 3% after five minutes at the same firing temperature. This confirms the idea that as water is driven off as steam it generates a pressure within the capillary pores which bloats the specimen. At 1440°C for the 10% addition, on heating for 7 hours the shrinkage overcomes the expansion and sintering occurs. For the 5% addition with a lower water content, the temperature and time required to start sintering is lower. As sodium silicate absorbs water so readily, it was found even after storing in a dessicator with silica gel that a large amount of water was absorbed (1.8%) .

TABLE VIISilica Analysis of Sodium Silicate

% SiO ₂ as received	=	36.80%
Loss on ignition	=	18.6%
(1 hour at 700°C)		
% SiO ₂ corrected	=	45.20%
% SiO ₂ corrected for		
5% excess Na ₂ O added	=	46.8%

Figs. 25 - 27, pages 112, 113 show the grain growth of the alumina with 5%.. and 10% additions compared with pure alumina, confirming the work of Price, Smithells and Williams⁽⁴⁹⁾.

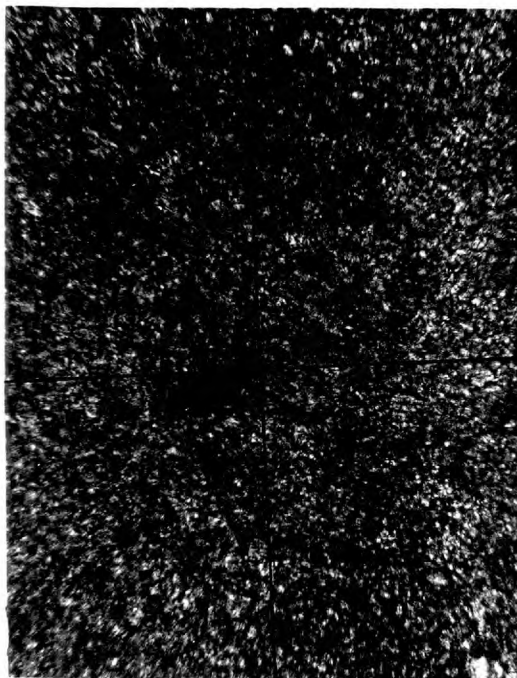


Fig. 25. Thin section of Alumina with 1%
addition of Sodium Silicate, sintered at
1550°C. for 90 mins. (x400)

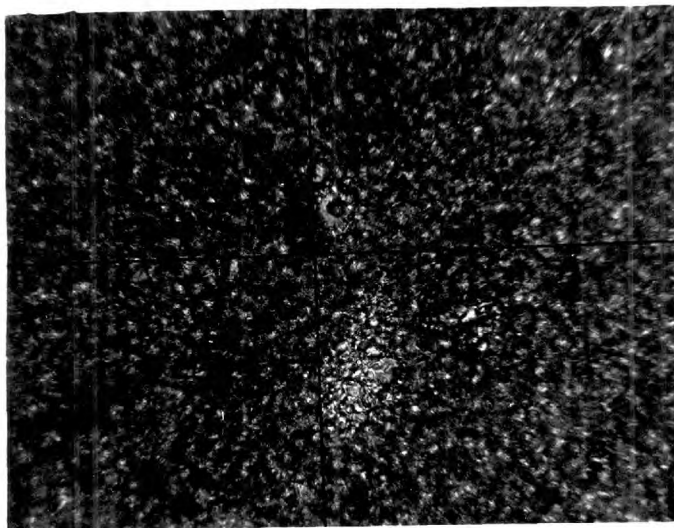


Fig. 26. Thin section of Alumina with 5% addition of Sodium Silicate, sintered at 1545°C . for 6 hrs. (x400)



FIG. 27. Thin section of Alumina with 10% Sodium Silicate addition sintered at 1600°C for 10 hrs. (X 400)

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