THE REMOVAL OF TEMPORARY ORGANIC BINDER FROM VITREOUS SILICON CARBIDE GRINDING WHEELS DURING FIRING.

PETER. YOUNG. MARCH, 1969. MASTER OF SCIENCE UNIVERSITY OF ASTON IN BIRHINGHAM.

Thereo 621.922 100

14.02071 145672

SYNOPSIS.

During the firing of vitreous silicon carbide grinding wheels, two defects can develop, viz. a resilient shiny black core, and a friable matt black core which seriously affects the strength.

The matt black core is probably due to the incomplete removal of temporary organic binder but earlier attempts to study this aspect have not been successful.

From a rigorous thermodynamic treatment, which necessitated the use of a digital computer, silica was shown to be a likely product of oxidation. In the absence of silicon, carbon tends to form in a closed system. At 1400°C and above, carbon is oxidised by silicat and at higher temperatures it oxidises silicon carbide to siliconmonoxide and carbon momoxide.

From the thermogravimetric experiments, binder removal was shown to occur in four stages viz. drying, dehydration, further decomposition or caramelisation, and oxidation. Dehydration was found to be particularly important, it is associated with dilation which affects porosity and morphology of the carbon residue to be oxidized.

/Contid. ii.

20

Oxidation was shown to occur in three stages using visual examination of pellets containing binder, high temperature bond and abrasive. The first stage was associated with non-wetting of the abrasive by the bond which produced the friable matt black core. The second was the removal of binder carbon entrapped in the bond, and the third was the removal of carbon from partial silicon carbide oxidation shown to occur at low oxygen potential.

It is suggested that future work is along the following lines: continuation of the small scale type of tests employed in this project: a study of heat and mass flow using a computer (either digital or analogue) and larger scale tests, to find the minimum time necessary at optimum burn-out temperature for complete carboh removal under production conditions.

110

	SYNOPSIS	- ii
4	INTRODUCTION	1
	i.i Grinding wheel manufacture	1
	1.2 Defects in finished products	1
	1.3 The oxidation of silicon carbide	2
	1.4 The use of organic temporary binder	9
	1.5 Carbon morphology	10
	1.6 Carbon burn-out	11
	1.7 Statement of problem	12
2	EXPERIMENTAL PROCEDURE	13
	2.1 Thermobalance work	13
	2.2 Visual examination of isothermally fired pell	ets 15
	2.3 Compressive strength tests	18
	2.4 Material selection	18
	2.5 Segregation experiments	20
	2.6 Heat transfer experiments	20
	2.7 Thermodynamic treatment of silicon carbide	21
	cridation using a digital computer	
3	RESULTS	27
	3.1 Binder pyrolysis	27
	3.2 Silicon carbide oxidation	30
	3.3 Microscopic exemination of isothermally fired pellets	32
	3.4 Strength tests on fired pellets	35
	3.5. Silo experiment	35

	5.6 Eent transfer	35
4	THERMODYNAMICS	39
	4.1 The nature of the problem	39
	4.2 Assumptions	40
	4.3 Method	41
	4.4 System I - silicon carbide/gas	45
	4.5 System II - SiC/SiO2/gas	51
	4.6 System III - SiC/Si/gas	55
	4.7 System IV - SiC/Si/SiO ₂ /gas	57
	4.8 System V - SiC/SiO ₂ /C/gas	60
	4.9 Detailed discussion of thermodynamic tables	62
	4.10 Conclusions	74
5	DISCUSSION	82
	5.1 The pyrolysis of pure binders	84
	5.2 Binder morphology	91
	5.3 Dispersion	94
	5,4 Binder decomposition and oxidation in the system silicon carbide:bond:binder	97
	5.5 Abrasive oxidation experiments	101
	5.6 The effect of bond fusibility	105
	5.7 The kinetics of burn-out	109
	5.8 The thermodynamics of burn-out	121
ŧ	5 CONCLUSIONS	131
	6.1 Drying	132
	6.2 Dehydration	132
	6.3 Caramellisation	133

	6.4 Macroscopic oxidation	134
	6.5 Microscopic exidation	136
	6.6 Tertiary oxidation and thermodynamic considerations	137
7	FUTURE WORK	140
	7.i Development of small scale tests	140
	7.2 Heat and mass transfer	142
	7.3 Large scale tests	143
	APPENDIX	
	REFEGENCES	

1. INTRODUCTION AND LITERATURE SURVEY.

1.1 Grinding Wheel Manufacture.

In the manufacture of silicon carbide grinding wheels the closely sieved abrasive is mixed with water, low temperature binder and high temperature bond. The mixture is compacted to shape; slowly dried (for circa three days) and then fired.

1.2 Defects in Finished Products.

During the firing, two major defects can develop. The first is a shiny black discol cration as shown in figure 1.1: the defect does not appear to affect grinding performance of the finished wheel although it is disadvantageous for sales promotion. The second defect is far more serious and is the subject of this study. It consists of a matt black core surrounded by two zones; the inner is light coloured and the outer a dark band which merges into the normal abrasive colour. see figure 1.2. The matt black centre and the light coloured zones are both extremely friable and render the wheel dangerous in use although the dark zone resembles the shiny black defect. It is thought that this defect is caused by the presence of binder which has not been completely burnt out; the carbonaceous residue coats the abrasive and prevents wetting by the vitreous bond.



FIGURE 1.1 Silicon carbide grinding wheel showing "shiny block" defect



Silicon carbide grinding wheel showing "matt block" defect FIGURE 1.2

. 2 .

1.3 The Oridation of Silicon Carbide.

Thermodynamically silicon carbide is unstable in a number of atmospheres including oxygen since it is oxidised with a negative free energy change. Its apparent chemical stability in service is due to the slowness of reaction at normal temperatures. In the firing of abrasive silicon carbide wheels reaction rate increases and becomes an important factor.

The oxidation is similar to that of metals, in that oxidation produces a film of oxide on the surface. The theory of oxidation of metals has been studied in considerable detail and in particular Gulbransen gives a complete survey of mechanisms. The principle difference which makes direct comparison difficult, is that silicon carbide is a compound and each element forms two oxides.

Wiebke measured the oxidation of silicon carbide in oxygen using three methods: the quantity of carbon dioxide formed; weight changes; and silica determinations on the product. The reaction assumed in each case was :

$$SiC + 20 \rightarrow SiO + CO$$

2 2 2 2

The silicon carbide was prepared by first calcining then cleaning three times in an acid mixture (HF + H SO + HNO) and washing 2 4 3thoroughly. Grain diameters of 31_{AV} , 63_{AV} , 100_{PV} , 150_{PV} , 241_{PV} and 510_{PV} were studied at 1300° C, and 63_{PV} was also studied at 900 C, 1100 C and 1500 C. A large scatter in the results was apparent and each method gave a different result. However, the following conclusions were drawn: oxidation rate increases with temperature, but decreases with time interval, and reducing the grain size, ie: increasing the specific surface increases the rate of oxidation.

··· 7 ···

The decrease in oxidation rate with time, which many authors have reported, can be explained by the presence of a film of silicen which passivates the underlying silicon carbide. If oxidation results are plotted against the square root of time a straight line is produced thus leading to the equation :

$$\frac{P1}{P2} = \sqrt{\frac{61}{t2}}$$

Pl = oxidation produced in time, tl

P2 = " " t2

This equation can be derived theoretically as follows: if the controlling factor is the thickness of silica the rate of the reaction will be proportional to the diffusion gradient in the layer; since the boundary conditions on either side of the layer remain constant throughout the experiment, this gradient will be proportional to the thickness; the thickness will also be proportional to the mass; whence

$$\frac{dP}{dt} = \frac{k}{p}$$

k = constant.

Cross multiplying and integrating yields

 $\frac{p}{2} = k t + C$, integration constant,

but when t = 0; P = 0, therefore C = 0. Thus the ratio for times (1) and (2) is

- le -

$$\frac{P2}{P1} = \begin{bmatrix} t \\ 2 \\ t1 \end{bmatrix}$$

The parabolic law is not valid with cyclic heating, or heating at low pressures (below 0.1) or after heating at low temperatures for a period of time (eg at 900°C after 6 hours) int the Atwo deviations are demonstrated by Erwin³ and the third by Wiebke². In each case the oxidation rate becomes constant with time, probably due to the absence of protection by a growing film. Presumably, cyclic heating cracks the film by thermal stressing while the phenomenon found by Wiebke probably results from spontaneous shattering of the film by a build up of stress. The deviation at low pressure is probably caused by a change to gaseous silicon monoxide formation rather than silica formation.

In air, from which carbon dioxide and water vapour have been removed, silicon carbide behaves very similarly though the arate of oxidation is less. Erwin has shown that the activation energy in air is different to that in oxygen, being 50 kcals per mole in oxygen and 80 kcals per mole in air.

The oxidation of silicon carbide in the presence of 4 water vapour has been studied by several authors including Lea, Jorgensen and Wiebke . Their results differ considerably though all conclude that steam accelerates the rate of oxidation. The effect may be due to a modification in the morphology of the silica layer, possibly by hydrolysis, or the layer may be 4 volatilised - both these suggestions are made by Lea .

From the above it is obvious that silicon carbide 3 oxidation is more complex than metal oxidation. Erwin illustrates this with a list of six possible oxidation reactions and from these table 1.1 has been constituted.

Free energy data for the oxidation of silicon carbide				
Products	Standard free energy change @ 250 C		Standard f	ree energy
Oxidation	for 1 mole SiC	for 1 mole 02	for 1 mole SiC	for 1 mole
S10 + C0	- 279.2 ^H	- 139.6	- 215.4	- 107.7
S10 + C0	- 2177	- 145.1	- 187.2	- 124.8
Si0, + C	- 184.9	- 184.9	- 120.7	- 120.7
S10 + C0	- 110.1	- 73.4	- 144.5	- 96.3
S10 + C0	- 48.8	- 48.8	- 116.3	- 116.3
S10 + C	- 15.8	- 31.6	- 49.5	- 99.0
S1 + CO	- 81.9	- 81.9	- 86.5	- 86.5
Si + CO	- 20.4	- 40.8	- 58.3	- 116.6

TABLE 1.1

~ 5 ~

The asterisk indicates the most negative free energy change in the column and hence the most likely reaction under the appropriate conditions, assuming favourable kinetics. Thus, it can be seen that if sufficient oxygen is available (columns 2 and 4) silicon carbide may be oxidised completely to silica and carbon dioxide but if oxygen availability is limited (columns 3 and 5) the silicon may be fully oxidised but the carbon may not be and at low temperatures the carbon may not oxidise at all. However, the temperature at which the mechanism changes cannot be determined from this table.

From table 1.1 the thermodynamics of other reactions can be deduced, for example, the oxidation of silicon carbide by carbon dioxide which can proceed by two reactions viz: $\frac{\Delta G @ 25 C}{\Delta G @ 1627 C}$

 $sic + co \rightarrow sio + 2c - 90.6 - 26.0$

SiC + $3CO \rightarrow SiO + 4CO - 33.2 - 102.6$ both these reactions are thermodynamically possible since all the free energy changes are negative though at 25°C the complete reduction of carbon dioxide to carbon is more likely and at 1627°C the reduction to carbon monoxide is more likely; this is consistent with the previous discussion. Also, from the same table the oxidation by carbon monoxide can be deduced :

sic + 200 \rightarrow si0 + 30 $\triangle G @ 25 C = -119.3$ 2 $\triangle G @ 1627 C = + 12.3$

Thus, silicon carbide can be oxidised by carbon monoxide at 25 C

but not at 1627 C. Experimental work by Erwin conflicts with this at first sight, since he shows that at 1250 C and below, no reaction occurs between silicon carbide and carbon monoxide, but at 1300 C silicon carbide is blackened. If the discoloured silicon carbide is then heated in air its original colour is restored, though the appearance of the grain is slightly different to that of silicon carbide oxidised in air, the former being dull with a transluscent tint and the latter more iridescent. The blackening can be shown to be carbon by analysing the gaseous products after heating in air as reported by Balmforth . The question now arrises whether this carbon constitutes a separate phase or not. If it does not form a separate phase, but dissolves into the silicon carbide, it is difficult to see why the appearance should be different after subsequent oxidation in air from silicon carbide not previously blackened.

The apparent discrepancy between the thermodynamic data given by Erwin and his experimental results on blackening must be due to kinetic rather than thermodynamic factors and may involve the activation of carbon nucleation as a controlling factor. These reactions are important in practice since silicon carbide abrasives are often made in gas fired kilns. In such equipment, water (already discussed above) will be present, together with carbon dioxide, and sometimes carbon monoxide.

Only pure silicon carbide has been considered so far but in vitreous silicon carbide wheels the presence of a glass Will influence the oxidation rate. Erwin found that glass

7 ...

accelerates oxidation rates up to 100 times and quotes activation energy of oxidation in oxygen in contact with No.4 SiO as being 28 kcals per mole. The vitreous bond 2 also affects permeability; increasing both the proportion used and its fusibility tends to reduce permeability.

Work has been carried out on the effects of this by Katz and Kajnorshii . There is still much work to be done in this field though the conclusion is that slight changes in permeability can have a large effect on oxidation rate. It is important to note that permeability changes during firing as a result of bond fusion, also the volume of gas increases with temperature (at 1400 C for an example an ideal gas expands about 6 times) while viscosity of gas increases about 8% each of these factors tends to inhibit gaseous mass transfer - and as shown by table 1.1 (column 3) restricted oxidation can lead to carbon precipitation. In addition permeability is affected by compacting pressure, grain shape and grain size distribution, although it is not directly related to porosity.

From table 1.1 it would appear that silica is the most likely oxide of silicon to form by oxidation and this has so far been assumed.

However, the possibility of silicon monoxide formation 9 should not be overlooked. Chapman using a Knudsen cell with thermogravimetric analysis has shown that silicon monoxide exists Cont'd.

- 8 -

at unit atmospheric pressure as a stable gas phase at and above 1200°C and thus its formation may contribute to the exidation mechanism at higher temperatures perhaps where exygen availability is limited. In table 1.1 column 5 the free energies of the reactions yielding silicon monoxide are not very much lower than those yielding silica; furthermore if the activities of the silicon monoxide can be reduced by dilution with carbon monoxide, carbon dioxide and atmospheric netrogen those reactions which form silicon monoxide could be promoted.

1.4 The Use of Organic Temporary Binder.

A complication to the system arises from the use of organic temporary binders (used to increase green strength) which are generally carbohydrates. Over the last 10 years a number of authors have examined the pyrolysis of carbohydrates, 10 ll l2 l3 for example Greenwood , Gardiner , Bloede , and Pictet . Initially water is lost forming a glucosan. With further heating decomposition proceeds with loss of more water and the evolution of carbon monoxide, carbon dioxide and several 10 hydrocarbons. Greenwood using gas chromatography has identified the following : Acetaldehyde, furan, 2methylfuran, methone, methylaldehyde, pentanol, 2- pentanone, 3- pentanone and 2.5 - dimethylfuran. The solid rechine becomes progressively richer in carbon. Initially caramel is formed, but as the distillation proceeds, the molecular structure

Cont'd.

- 9 -

becomes extremely complex and uncertain. Eventually a state is reached which, for this thesis, can be considered as elementary carbon.

The evolution of water, carbon monoxide and carbon dioxide has already been discussed. The effect of the hydrocarbons is difficult to assess, they will probably result in little or no oxidation of the silicon carbide but their formation is useful to the extent that they assist in the removal of binder, but disadvantageous to the extent that the carbonaceous residue which is left may be difficult to remove later and may even become entrapped by the glass/silicon carbide structure.

It has been deduced from table 1.1 (and the reaction between silicon carbide and carbon monoxide) that carbon is stable at and below 1300°C if the oxygen supply is restricted, thus under these conditions residual carbon from the binder will not burn out. It may therefore be concluded that sufficient oxygen must be available. However, the problem is more complicated than this treatment indicates since Balmforth using oxidising agents to assist carbon removal found that they had little or no beheficial effect and in some cases appeared to increase discoloration.

1.5 Carbon Morphology.

So far two forms of carbon have been considered: firstly arising from the partial oxidation of silicon carbide, and

Cont'd.

-- 10 --

secondly from incomplete removal of binders. It seems likely that these two forms of carbon are responsible for the two types of defect - the first producing the shiny black defect and the latter the friable matt black defect. It is also important to note that the silica produced by the oxidation of silicon carbide will affect the final composition of the bond.

1.6 Carbon Burn-out.

made an investigation in which an attempt was Biggin made to avoid the development of friable black cores during firing (believed to result from binder carbon) by determining critical production parameters within which they do not occur. These parameters were grit size, wheel grade, wheel size and firing cycle. Grit size and grade were considered as limiting factors because of their effect on wheel structure. Grit size has an influence on packing density while grit and grade together define within fairly close limits the fusibility and amount of high temperature bond. Grade also controls the compacting pressure and the porosity of the wheel structure. Grit and grade were varied over a wide range, the largest grit being 16 mesh and the finest 80 mesh in grades K (soft) through to S (hard). Wheel size in thickness from 2" to 7" deep and all 24" diameter. The firing cycle was restricted to the faster 5-day kilns since it is in such kilns that burn-out trouble occurs. The results of these tests may be summarised as follows:

Cont'd. .

- If an inert abrasive is used (ie: alumina abrasive)
 it is found that :
 - A) all 2" thick wheels can be fired satisfactorily,
 - B) all wheels 6" and deeper suffer from matt black cores,
 - C) 4" wheels in the coarser grits can be fired satisfactorily but not in the finer grits, though the critical grain size below which trouble is avoided varies with grade - this is shown in figure 1.3.
- When silicon carbide wheels were used no useful conclusions could be drawn and consequently only a few very small products are fired on 5-day kilns.

1.7 Statement of Problem.

Up to the present the firing technique for silicon carbide wheels has been determined by trial and error only and the amount of progress that can be achieved in this way has now reached its limit; further improvement requires a fundamental study of the problem but there has been very little work of this type done. In this project an attempt is made to determine some of the fundamental parameters concerning the thermochemistry of firing silicon carbide in contact with temporary binder and high temperature bond, with the aim of rationalising the firing process.

HIGH TEMP. BAUXILITE BLACK CENTRE, PREDICTION CHART.

UNIFORM BLUE COLOUR OF FIRED BAUXILITE.



BLACK CENTRE OFTEN ASSOCIATED WITH SOFTNESS.

FIGURE 1.3

2.1 Thermobalance Work.

The thermobalance was the only special apparatus used in the project and it was used for research which required direct measurement of weight changes during oxidation experiments. It consisted of a vertical tube resistance furnace mounted over an automatic analytical balance and the apparatus was equipped with a recorder which gave continuous graphical output of temperature and weight of sample. A photograph is shown in figure 2.1.

The furnace had an internal diameter of 2", it was wound noninductively with nichrome wire and capable of operating up to 1000°C. The furnace temperature could theoretically be programmed to give a linear rise from room temperature to the operating maximum though some deviations were encountered below 200°C, especially with very slow heating rates. The top of the furnace was plugged to prevent through convection as this would seriously affect weight measurement, but the bottom was left open to allow free movement of the sample support rod. The furnace was supported by pulleys to allow free vertical movement.

The balance had two pans for increased accuracy and to the rear pan a support rod was attached which projected up into the furnace. The rod was positioned to support a sample in the



centre of the furnace when the latter was fully lowered. The balance capacity was 100 grams and the automatic control acted over a range of -1 gram by changes of 100 milligrammes to the rear pan.

The sim of the thermobalance work was to obtain basic information. For this reason oxidation studies in air at unit atmosphere pressure were performed on binders and on silicon carbide abrasive both separately and in combination. It was thought that this approach would give information which could then be used to interpret more complex systems that contained a high temperature bond.

fhe thermobalance weight/temperature record chart was used as the main source of information (see appendix) although some weighing of samples before and after testing was also employed and visual examination was employed.

All the binder oxidation tests were carried out on the thermobalance using an open 32mm diameter silica crucible. Initially samples of 1 gm. were used although some tests had to be repeated using ½ gm. samples owing to excessive expansions of binders which produced spurious readings. All tests were started at room temperature and most were stopped at 600°C since it was concluded from early results that oxidation was complete by this temperature though a few tests were taken to 1000°C while some were stopped below 600°C to allow visual Cont'd. examination of the partially oxidised material. The binders used were starch, dextrin and glucose.

Similar experiments were performed on binder/abrasive/ water mixings in which all the binders were tested but only 46 mesh silicon carbide was used. Two tests were also run on pellets containing starch, water, bond and abrasive under a programmed temperature rise and secondly isothermally at 1000°C.

The thermogravimetric experiments on silicon carbide were made on 10 gm. samples of 46 mesh green abrasive using the 32 mm. crucible open, and two types of test were performed. The first involved programmed heating up to 1000°C; in the second series of tests isothermal firing was used and temperatures of 500 to 850°C were examined in increments of 50°.

2.2. Visuel Examination of Isothermally Fired Pellets.

The principal aim of this series of experiments was to investigate the effect of bond. To do this pellets were prepared and isothermally fired for a timed period, sectioned and examined visually.

Small pellets were chosen for the following reasons: they can be prepared, fired and examined easily using small scale laboratory equipment; they can withstand rapid temperature changes; and, related to this, the centre temperature approaches the surface temperature rapidly thus permitting a fair

approximation to true isothermal conditions.

Sectioning was necessary to allow inspection of the structure at the centre of the pellet.

- 16 -

Isothermal firing was employed for the following two reasons: firstly, the technique is simple to use and since it does not require temperature programming the two parameters time and temperature can be varied easily and accurately over wide and finely divided ranges; secondly, the historic effect of heating at different temperatures is theoretically eliminated and in particular the possibility of entrapping carbon by fusion of the bond can be examined - if programmed heating is used the binder can burn out before the bond has fused on small samples. The firing was performed in a small resistance heated muffle furnace. The pellets were fired individually.

In this series of experiments two abrasives were used viz. 46 mesh green silicon carbide and 120 mesh white alumina. The latter was introduced to examine the effect of bond on binder burn-out independently of silicon carbide oxidation; these tests were carried out over a lower temperature range and with a number of different bonds. The reason for using a finer grain in the alumina work followed from the objective which was to study entrapment; it was felt that the effect would show more clearly using a finer grain size which was also the reason for using white alumina rather than brown: had the alumina tests

been carried out first it might have been sensible to use 120 mesh silicon carbide though comparison would still have been hampered severely by the fact that different bond systems are used in silicon carbide wheels. However, the task undertaken in this project is to elucidate the mechanisms involved in firing; once this has been achieved the work can be extended by measuring the required parameters on all bond systems. The choice of 46 mesh in the silicon carbide abrasive was based on the following reasons: it is an intermediate grain size in the precision range, and it was used extensively in the thermogravimetric work, section 2.1.

The pellets were prepared by thoroughly mixing abrasive, bond and water so that the binder and water were evenly spread over the surface of the grains. The bond was then added and mixing continued to allow the bond to adhere to the wet surface of the grains producing a very even coating of binder, bond and water. The pellets were compacted in two ways: those containing silicon carbide were produced individually by pressing into a $\frac{2}{7}$ diameter cylindrical mould using enough mixing to produce a pellet approximately $\frac{2}{7}$ long; the alumina pellets, however, were pressed in square bars measuring 6 x 1 x 1" and then sectioned into five 1" cubes - $\frac{1}{7}$ " was removed from each end to eliminate end skin effects. Both silicon carbide and alumina pellets were pressed to 2 t.s.i. and after pressing they were dried at 110°C for 24 hours. Compositions are given under

- 17 -

"Material Selection", section 2.4, together with bond softening temperatures.

Sectioning the alumina pellets was performed mainly with a hack saw though some of the pellets fired at higher temperatures were slit on a diamond wheel using water as a coolant. The silicon carbide pellets did not section successfully in these ways, the hack saw method was quite inadequate and the slitting wheel produced surface effects that made interpretation difficult. Therefore, the silicon carbide pellets were broken into two (or more) pieces 4 carefully hammering the cylindrical pellets on a hard surface usually produced a clean fracture through the centre parallel to the length.

2.3. Compressive Strength Tests.

These tests were carried out on a small compressive strength testing machine to supplement the visual and thermogravimetric examination of silicon carbide, for this a few extra pellets were fired at 1000 C.

2.4. Material Selection.

All materials were supplied by Universal Grinding Wheel Co. Ltd., It was decided not to use specifically high purity chemicals but those used in the industry since the two might have different properties and this could be misleading. All materials were stored in a cool dry place.

- 18 -

The low temperature binders chosen were the hydrocarbons starch, dextrine and glucose and the abrasives used were green silicon carbide and white alumina these being about 99.5% pure. The high temperature bonds used are listed in table 2.1. and in table 2.2. are given the compositions of mixtures used to make pellets.

Bond Designation	ARF	CRR	RF	RE
S10 -	68.1	73.0	69.7	69.8
Tio		0.2	0.5	0.5
A1 0	23.7	14.8	17.6	15.0
23 Fe O	0.2	0.3	0.5	0.4
B 0		3.7	2.6	5.6
2 3 CaO	0.4	0.4	1.2	0.7
MgO	0.1	0.1	0.3	0.2
KO	4.9	4.0	3.9	?
NaO	-	3.4	3.2	} 7.0
P 0 2 5	-	-	0.5	0,2
Softening Temperature	1340	1240	1200	1150
Water content	3.90	2.68	2.82	3.29
Clay content(nominal)	30	22.5	24	27
Flux content(") 0	22.5	27	57.5

(The data for this table was obtained from Universal Grinding Wheel Co. Ltd.,)

		and the second
Composition of	of Mixings Used	in Pellets.
Per 100 Parts Abrasive	SiC Pellets	Al O Pellets 2 3
Bond	20	.30
Dextrin (binder)	2	2
Water	6	4

Table 2.2.

20 -

2.5 Segregation Experiments.

All abrasives used in this project were taken from silo storage and it was thought that this might introduce errors due to segregation within the silo. In order to test this a small scale simulation experiment was performed as follows: a 5 litre glass beaker from which the bottom had been removed was attached to a large funnel; the whole apparatus was filled with 7 kgm. of 22 mesh silicon carbide abrasive and samples were drawn off, screened and weighed.

2.6. Heat Transfer Experiment.

A large portion of the experiments performed in this project involved isothermal firing. However, time is required for heat transfer to occur and therefore some estimate was made to show how rapidly temperature rises in the pellet to that of the furnace. To estimate this a number of inch cubes in alumina, not used in the burn-out work, were heated for a Cont'd. timed period of up to 1 hour and then plunged into a water calorimeter. The resultant temperature rise was noted and divided by sample weight to obtain a measure of the average pellet temperature. In the case of silicon carbide heat will be transferred more quickly partly because of its higher surface emissivity and partly because of its thermal diffusivy is approximately three times that of alumina.

2.7. The Thermodynamic Treatment of Silicon Carbide

Oxidation Using a Digital Computer.

In section 4 the equilibrium states of five different systems are considered using thermodynamic and stoichiometric equations. The solutions of these equations is very complex, in some cases, and requiring iterative solutions and it was therefore necessary to use a digital computer to perform the necessary calculations. Since this aspect of the project is intended to generate rather than process information it was felt that the programming of the computer could be treated as part of the experimental procedure and it is therefore included here.

Most of the task of computing is common to all five sets of calculations and use was made, therefore, of the procedure PRECOMPILE. One part, which will be called the master programme, was written with all the common operations, processed and then output in sum checked binary. To examine

Cont'd.

- 21 -

any particular system the master programme was then read in at speed followed by a slave programme containing those calculations peculiar to the system.

The master programme, shown in figure 2.2. is mainly an input and output routine which uses information supplied by the slave programmes, and it has been divided into four sections.

Section 1 of the master programme, is a setting up stege and in this section the identifiers, shown in table 2.3. are declared. The first three statements specify output format while the next three determine, in degrees Kelvin, the temperatures for which calculating are required. I is a switch identifier subscript; it is set equal to 2 so that subsequent return from a slave programme will be at the next print statement labelled START 2. Exit from the master programme is then caused by an unconditional transfer statement.

Section 2 of the master programme is an output section which handles the table heading operation and it is entered on the first return from a slave programme. The leading statement outpubs a title and a statement which partly defines the system. The definition is completed by the next five statements some of which are conditional and controlled by values assigned to Cl, Sl and S2 in the slave programme. Column headings are then printed, and again some of the statements are conditional, following a pattern similar to that used to specify the system.

Cont'd.

- 22 -

EQULIBRIUM PARTIAL PRESSURE CALCULATION BEGIN REAL PO2, PC02, PC0, PSIO, PTOT, PN2, NSI, NSIC, NSIO2" INTEGER T.DT.TM. I BOOLEAN C1.S1.S2 SWITCH -SS: =START1, START2, REP, CALC PREFIXCE 1) SCALED(3) DIGITS(4) READ T. DT. TM T:=T+273' TM:=TM+273 11=21 GOTO START1 COMMENT END OF SECTION 1" START2: PRINT EELS12? TABLE?, EES2R3? . ER2S2R15? SHOWING EQ?, CUILIBRIUM CONDITIONS FOR THE SYSTEM SIC/02?" IF S2 THEN PRINT E/S102? PRINT £/SIO? IF S1 THEN PRINT E/SI?" PRINT £/CO2/CO7 IF C1 THEN PRINT £/C? P(\$10) P(N2) 7, PCCO20 PCCOD PRINT EEL3S127P(02+R) T ?" E PCTOTO NCC37 IF C1 THEN PRINT £ IF S1 THEN -PRINT C NCSID?" PRINT & NCSICO?" IF S2 THEN PRINT & N(S102)?" PRINT & NCO2.1) 7 ACC2? IF NOT C1 THEN PRINT C -ACS10?" IF NOT ST THEN PRINT £ AC\$10227 IF NOT S2 THEN PRINT £ PRINT EEL2?? 1:=3 COMMENT END OF SECTION 2" REP: PRINT £ES10??, PO2, PC02, PC0, PSIO, ALIGNEDC1, 30, PN2, FREEPOINT(3), PTOT, £ -?, T-273, £ ? NSI02+=(0.25+PN2-PC02-P02-0.5+PS10-0.5+PC0)/PTOT NS1:=(2*PC02+1.5*PC0+P02-0.5*PS10-0.25*PN2)/PTOT ALIGNED(1,3) IF C1 THEN PRINT £ ?, SPECIAL(2), -NSI IF S1 THEN PRINT & 7, SPECIAL(2), NSI ELSE NSI =0 PRINT £ 7, SPECIAL(2), -(NSI02+PSI0/PTOT+NSI) IF S2 THEN PRINT £ 7, SPECIAL(2), NSI02 PRINT £ 7, SPECIAL(2), -PN2/4/PTOT, £ 7 SCALED(3) SCALED(3) IF NOT C1 THEN PRINT EXP(20533/T-20.94)/PC02.PC0.PC0 IF NOT S1 THEN PRINT EXPC-11646/T-10+12) PSIO/SQRT(PO2) IF NOT S2 THEN PRINT EXP(93880/T-31.4) PSID SQRT(PO2) PRINT ££L2?? COMMENT END OF SECTION 3" T:=T+DT' IF (T+SIGN(DT)) LESSEQ (TM+SIGN(DT)) THEN GOTO CALC* PRINT CER100LS127P = PARTIAL PRESSURE IN ATMOS. T = TEMP? CERATURE IN DEG.C. A = ACTIVITY OF SOLID PHASESELT?, EES12?N = MOLES-OF REACTANT OR PRODUCT PER MOLE OF GAS PHASE?, £ CREACT. -VE : PROD. +VEDELR100??, EER100?? ELLIOTT (7,0,00,0,0,0,0,00) ELLIOTTC7, 3, 04, 1, 1, 6, 01) START1: ELLIOTTCO, 0, 00, 0, 0, 0, 000 COMMENT END OF SECTION 4 PRECOMPILE

FIGURE 2.2 The master programme

Before this section is left lis changed to 3 so that on all subsequent returns from the slave programme entrance occurs at the statement labelled REP which heads section 3.

In section 3 the partial pressures, calculated in the slave programme, are printed. Molar yields and activities are calculated and printed, using conditional statements which follow the same pattern as in section 2. However, the molar yield of carbon is not calculated separately since from section 4

> N = NC (NSI=0) Si (NC=0)

T.ahal	Type	Function
P02	Real	Partial pressure of oxygen
PC02	11	" carbon dioxide
PCO	11	" carbon monoxide
PSIO	11	" silicon monoxide
PN2	н	" nitrogen
PTOT	tf	Total pressure of system
NSI	u	Moler yield of silicon
NSIC	п	" silicon carbide
NSI02	n	" silica
T	Integer	Absolute temperature
DT. TM	11	Temperature control constants
C1.	Boolean	Carbon is included in system
S1	11	Silicon " "
\$2	15	Silice " "

Table 2.3.

Section 4 is entered after exit from section 3 end it is basically a control routine:. The current temperature, T, is raised by DT and compared with TM; if it is in range, control is transferred back to the slave programme; if it is out of range the programme is terminated, this consists of first outputting a footnote, and secondly executing an instruction read in from the word generator which is usually an instruction to read at speed the precompiled master programme in preparation for the slave programme of the next system.

- 24 -

The slave programmes are shown in figures 2.3 to 2.7 and in each of these the following three operations are performed: firstly the system is defined; secondly the equilibrium partial pressures of the gaseous components of the system are calculated for one temperature; and thirdly control is transferred back to the master programme using subscripted switch identifier SS.

The formula used in the slave programmes are taken from section 4 where they were derived.

```
COMMENT SIC/02 = S10/C02/C0'
C1:=S1:=S2:=FALSE
CALC:
BEGIN REAL A, B, KA, V
      OWN REAL X
      BOOLEAN LOW!
      REAL PROCEDURE F(A,B,C)'
VALUE A,B,C' REAL A,B,C'
BEGIN REAL N'
             N:=LN(C)+A'
             F:=EXPCIF N GR 170 THEN 170 ELSE N)
      END'
       1F 1=2 THEN X:=1'
      A: =-49290/T+42.325'
      B: =-67940/T+20. 835'
      KA: =EXP(-A)'
      FOR V:=0,
               X WHILE LOW,
               x/2,
v/2 while v/x GR 0-5 DO
       BEGIN X:=CIF LOW THEN V ELSE -V)+X'
             PC02:=CX**3+SQRTCX**0+4*FCA,4,X)))*0.5*KA'
             P02:=F(B,2,PC02/X)'
             PTOT: =8*PC02+5*P02+6*X'
             LOW: =PTOT LESS 1
       END'
       PCO:=X '
       PS10:=PC02+PC0'
       PN2:=PTOT-PO2-2*PS10*
       GOTO SS(1)
```

```
END'
```

FIGURE 2.3 Slave programme for the solution of system I

```
COMMENT SIC/02 = S102/S10/C02/C0'
S2: =TRUE
C1: =S1: =FALSE *
CALC:
BEGIN REAL A, B, C, V '
OWN REAL X
       BOOLEAN LOW
       REAL PROCEDURE F(A,B,C)'
VALUE A,B,C' REAL A,B,C'
BEGIN REAL N'
               N:=LNCC)+A'
               F:=EXPCIF N GR 170 THEN 170 ELSE N)
       END '
       IF I=2 THEN X:=1"
       A:=146500/T-20.332"
       B:=112530/T-9.912'
       C:=31.40-93580/T'
       FOR V:=0,
                X WHILE LOW,
       X/2,
V/2 WHILE V/X GR 0-5 DO
BEGIN X:=CIF LOW THEN V ELSE -V)+X'
               PCO2:=F(A,2,X)'
PCO:=F(B,1.5,X)'
               PS10:=F(C,-0.5,X)'
               PTOT:=5*X+9*PC02+7*PC0-PS10'
               PN2:=(4*X+8*PC02+6*PC0)-2*PS10"
               LOW: =PTOT LESS 1 OR PN2 LESS 0
        END!
        P02:=X'
        GOTO SS(1)
END
END'
```

FIGURE 2.4 Slave programme for the solution of system II
```
COMMENT SIC/02 = SI02/SI0/C02/C0/C*
     C1:=S2:=TRUE
     S1:=FALSE
CALC: PO2: =EXP(-99093/T+20. 432)
     PC02:=EXP(-51686/T+20.532)
     PCO:=EXPC-36110/T+20.7363
     PS10:=EXP(-44334/T+21.184)
     PTOT:=PC02+PC0+PSI0+P02*
     IF PTOT LESS 1 THEN PTOT =1
                                         FIGURE 2.7
     PN2:=PTOT-PC02-PC0-PS10-P02
     GOTO SS(1)
```

Slave programme for the solution of system IV

) END

```
COMMENT SIC/02 = SI02/SI0/SI/C02/C0"
     S2:=S1:=TRUE
     C1:=FALSE
CALC: PO2:=EXP(-105526/T+21.28)"
     PC02:=EXP(-64552/T+22.228)
     PCO:=EXP(-45759/T+22.008)
                                     FIGURE 2.6
     PS10:=EXPC+41117/T+20.76)
     PTOT:=PC02+PC0+PSI0+P02
     IF PTOT LESS 1 THEN PTOT =1
     PN2: =PTOT-CPC02+PC0+PSI0+P020
     GOTO SS(1)
```

END END '

S1: =TRUE '

CALC:

C1: =S2: =FALSE '

```
BEGIN REAL KA, KB, KC, A, B, DIS, RX'
      KA:=EXP(40976/T+0.96)
      KB:=EXP(7006/T+11.37)'
      KC:=EXP(11646/T+10.12)
      A:=(KA+1)*5"
      B:=(KB+KC)*3
      DIS:=B*B+4*A'
      RX:=(-B+SORT(DIS))/A/2"
      PO2:=RX*RX'
      PC02: = P02*KA
      PCO: =RX*KB
      PSIO:=RX*KC
      PTOT: =PC02+PC0+PS10+P02'
      IF PTOT LESS 1 THEN PTOT := 1'
      PN2:=PTOT-PO2-PCO2-PCO-PSIO
      GOTO SS(1)
          Slave programme for the solution of system III
```

COMMENT S1C/02 = S10/S1/C02.'CO'

FIGURE 2.5

END

- 25 -

Table 2.4

Label	Type	Function
V	Real	Partial pressure range
Х	u	Iterated partial pressure
A,B,C	п	The second second second
KA,KB,KC	11	Constants
RX,DIS	11	
LOW	Boolean	PTOT 1 or PN2 0

The analytical calculations require minor transliterations only from algebraic to algorithmic form though the iterative calculations require further explanation.

In all iterative solutions a FOR loop is used. Before it is entered a number of identifiers shown in table 2.4. that are to be used in the loop, are declared. Among these is the OWN REAL identifier X which is initially defined by a conditional assignment statement. Also a REAL PROCEDURE F is declared which evaluates expressions of the form

with a minimum likelihood of overflow. A few constants are then calculated and the FOR loop is entered where X is iterated over the range -V.

Cont'd..

The first cycle of the FOR loop defines LOW for current values of X and T. For the second cycle and all subsequent cycles, while the value of LOW remains true the range is doubled. When this element in the FOR list is exhausted (ie: when LOW is false) the third element defines V, the fourth element then closes the range in conjunction with the leading IF clause in each loop. Iteration continues until accuracy is better than four figures.

3. RESULTS.

- 27 -

The results of the experimental work may be divided into five sections. In the first (section 3.1) the three binders, starch, dextrin and glucose, are examined by pyrolysis at a programmed temperature rise using the thermobalance. Followed by the pyrolysis of binder/abrasive mixings and one binder/abrasive/bond mixing. In addition binder pyrolyses were stopped at various temperatures to allow visual examination of the partially decomposed binder. In section 3.2, experiments to examine the oxidation properties of silicon carbide are reported, using the same apparatus, although particular attention is paid to isothermal firing. In section 3.3, the results of firing isothermally pellets of silicon carbide, bond and binder, and pellets of alumina, bond and binder are presented. Fourthly, a series of ad hoc experiments were performed and these are reported in sections 3.4, 3.5 and 3.6. The final part of the investigation consisted of a theoretical analysis of the oxidation of silicon carbide in air using a digital computer and this is reported in section 4.

3.1 Binder Pyrolysis.

The calculations necessary to transfer the result of pyrolysis recorded on the thermobalance output chart were calculated as follows: the origin on the thermobalance output

Cont'd.

chart was taken as 100% and the weight per cent of the semple was calculated from this point. In each of these figures the abscissa is temperature and the rate of heating was approximately 50 C per hour except in the case of one test performed on dried glucose where a very rapid heating rate of ca 300 C per hour was used. Most of the tests took 14 hours to complete. Since the temperature was programmed at a finite heating rate the temperatures recorded at which rapid changes in weight occur are probably higher than those that would have been obtained had either a very much slower heating been used or a series of isothermal firings to constant weight been used although both these methods would have been much more protracted - to take an example, drying will proceed at Arom 100 C if sufficient time is allowed but the results of these experiments it is indicated that drying is not complete until 120 C. this temperature head of 20 is presumably necessary to transfer heat from the furnace to the crucible and into the mass of binder.

The results of pyrolysis up to 700 C are given in figures 3.1.1 to 3.1.3 for each binder. In figure 3.1.4 the pyrolysis on a sample of dried glucose is shown and it can be seen that there was no drying stage. In figures 3.1.5 and 3.1.6 the results of pyrolysis on larger samples of glucose and dextrin are given which show an apparent increase in weight Cont'd.

- 28 -



FIGURE 3.1.1



FIGURE 3.1.2



FIGURE 3.1.3







FIGURE 3.1.6





following a rapid weight loss; this anomalous behaviour was the result of very large dilations of the binders causing them to protrude above the crucible top and touch the furnace wall thus disturbing the weight record - starch did not show this effect. Figures 3.2.1. and 3.2.2. show the state of the binders at three different temperatures, they were produced by discontinuing the pyrolysis at the temperatures stated. Starch remained compact and similar in appearance to dextrin heated to 220°C.

The pyrolysis of pure binder differs from practice in two very significant ways: first, the binder is finely dispersed in a wheel and not concentrated in one area, and second, the bond and abrasive can impede oxygen transfer to the binder. To investigate the effect of dispersion, tests were run on binder/abrasive mixtures and the results are shown in figures 3.3.1 to 3.3.3. The heating rate used was the same as on the pure binders, ie: 50 per hour, and the method of calculating weight per cent is similar although the weight of binder was only a proportion of the total sample weight. Since water was added to facilitate mixing the initial weights were greater than 100%; however, due to evaporation they were less than might have been expected from the mixing compositions and consequently the minimum weight recorded after the completion of pyrolysis is assumed to be Cont'd.

- 29 -





FIGURE 3.3.2



FIGURE 3.3.3





190 . 5 Z. B.

zero, and all other percentages are calculated from this point (see appendix). To assist in the examination of the effect of bond two tests were run on a pellet containing starch, silicon carbide, bond and water. The first test followed the same programme as the binder/abrasive (only) tests and the result is shown in figure 3.4.1. although the second test, shown in figure 3.4.2, isothermal firing at 1000 C was used; in this graph the abscissa is time, and a logarithmic scale is used.

3.2 Silicon Carbide Oxidation.

The thermobalance work on binder pyrolysis was extended to study silicon carbide oxidation and two types of test were used, the results of which are shown in figures 3.5.1 and 3.5.3. In each of these figures the changes in weight as ppm of original sample weight is plotted either against temperature or time. Figure 3.5.1. shows the effect of programmed heating on silicon carbide while in figure 3.5.2 the effect of isothermally firing the same grit is shown.

In the first experiment the origin on the thermobalance output chart was assumed to be zero and weight change was calculated from this datum although in the second experiment a different technique was used.

For the results shown in figure 3.5.2. the thermobalance furnace was preheated and then lowered over the samples at

Cont'd.





FIGURE 3.5.2

temperature. This procedure produces strong convection currents which caused a rapid deflection in the weight recording. These currents, however, subsided as the crucible and sample attain temperature and it is observed that in all but the highest temperature tests the weight recording reaches a steady value within 4 minutes and this is maintained for varying lengths of time, the longest time being at the lowest temperature of 500 C, when it is just under 8 hours. The weight recorded after 4 minutes is higher than the recording before lowering the furnace and it is probably due to impingement of steady state confection on the base of the crucible: this weight plateau is therefore assumed to be zero and changes in weight are expressed as ppm of the original sample weight from this datum. For the higher. temperature tests, viz: 800 and above no plateau is observed. and therefore a datum is calculated by averaging the drop in weight recorded after the initial increase to the plateau observed below 800 C, (a correlation on this drop with temperature showed no significant relation). In this series of experiments, runs were also made on alumina and a sample of silicon carbide previously fired at the same temperature the latter curve is distinguished by an asterisk placed after the temperature designation.

Cont'd.

- 31 -

3.3. The Microscopic Examination of Isothermally Fired Pellets.

The results of these tests described in section 2.2 are shown in figures 3.6.1 to 3.7: figures 3.6.1 to 3.6.4 are contained in a pocket at the back of the thesis:

The silicon carbide results which are the main aspect of the thesis are shown actual size in figures 3.6.1 to 3.6.4. Four different compacting pressures were considered and four different temperatures covering the range 1250°C to 1400°C. These extended the thermobalance work. In the tests up to and including pellets fired for 1 minute, a total of four zones or structures can be distinguished, viz:

A .	Dark - friable	
в.	Light grey - friable	
C.	Black - hard	
D.	Green - hard	

After 20 seconds the specimens were dark brown and A was the predominant zone, although some B was visible mainly at corners. After 40 seconds many of the specimens showed all four zones although D only at corners in some cases - also A was then matt black. After 1 minute D was clearly distinguishable in most specimens and zone B tended to move nearer to the centre of the pellet. Subsequent firing eliminated the friable zones and in some cases only the hard green structure (D) was found. However, the photographs of Cont'd.

- 32 -

some of the pellets containing only the hard zones are rather deceptive: initially zone C, although it was quite distinct from A, tended to be slightly matt and this contrasted well against the surrounding D. With continued firing C became progressively more shiny and failed to contrast against the outer zone. Because of this effect a brief description of the hard structure pellets is given.

The results of firing pellets at 1250 C are shown in figure 3.6.1. Pellets fired at this temperature after compacting to 1.1. t.s.i achieved uniform green colour in 3 minutes. Those compacted to 2.2 t.s.i achieved this structure in 10 minutes; after 3 minutes a small triangular patch of zone C still remained. The pellets compacted to the higher pressures in both cases retained zone C up to 1½ hours although the area was no more than ½" across.

The results of firing pellets at 1300 C are shown in figure 3.6.2 in which zone C was more persistent. A border of D surrounded a core of C up to 1½ hours, 6 hours, 18 hours and 24 hours in pellets compacted to 1.1 t.s.i, 2.2 t.s.i, 4.5 t.s.i, and 5.6 t.s.i, respectively, with the exception of one pellet compacted to 1.1 t.s.i, and fired for 3 minutes. This pellet was uniformly green. The border of D was about 4" deep on pellets compacted to 1.1 t.s.i changing to ½" deep on pellets compacted to 5.6 t.s.i. However, the depth was Cont'd.

- 33 -



FIGURE 3.7 The isothermal firing of alumina pellets

affected little by time: the changes to uniform green were abrupt.

The pellets fired at 1350 C are shown in figure 3.6.3. These pellets when compacted to 1.1 t.s.i and 2.2. t.s.i retained zone C up to 20 minutes and 2½ hours while those compacted to higher pressures retained zone C up to 24 hours and the depth of D was about $\frac{1}{6}$ " deep - in the previous pressure range D was about $\frac{1}{4}$ " deep.

The pellets fired to 1400 C are shown in figure 3.6.4. Their structure in each case consisted of two zones of which the outer zone was essentially the same as the uniform green structure of the lower temperature tests except that the pores were more open - ie: the pellets had "boiled". The depth of D was about &" deep in pellets compacted to 1.1 t.s.i and fired up to 100 hours and in pellets compacted to 2.2 t.s.i and fired up to 100 hours. In pellets compacted to 4.5 t.s.i the zone was less than 1/16"up to 6 hours increasing to a" at 18 hours and longer. In pellets compacted to 5.6 hours the zones were less than 1/16" up to 18 hours becoming to at 50 and 100 hours. The centre zone was shiny black up to 18 hours; however, at 50 and 100 hours the centre zone was much paler being a grey/green colour and not obviously carbonaceous.

In figure 3.7 the alumina pellets are shown at less than actual size. Only one compacting pressure was used and the maximum temperature examined was 1200°C although from 300°C Cont'd.

- 34 -





to this temperature the range was well covered.

3.4 Strength Test on Fired Pellets.

Following the pyrolysis at 1000 C of pellets made from silicon carbide, binder and bond, and reported in section 3.1 figure 3.3; the samples were tested for compressive strength and the results are given in figure 3.8 where fracture stress in pounds/square inch is plotted against time using a logarithmic scale.

3.5 Silo Experiment.

The results of this experiment are shown graphically in figure 3.9 where the weight per cent of each fraction is recorded. This graph shows no overall tendency for the distribution of grit particle size to change with position in the sample and from this it is concluded that sampling from silo is sufficiently representative of the bulk material.

3.6 Heat Transfer.

The results of these experiments performed on alumina bond/binder pellets at Universal Grinding Wheel Co. Ltd., are shown graphically in figure 3.10. In this graph the function:

0 = <u>Rise in calorimeter temperature</u> x 100 (1) sample weight

Cont'd..



mers/20 at 0

is plotted against time, t. This function is proportional to the average temperature of the pellets and in the following treatment the time is found for this temperature to reach 90% of the equilibrium value, 0, reached after infinite soaking time in the furnace.

now and using the results at & minute -nt (t=0) using the nesults at & minute (4)

and the slope

If it is assumed that after 1 hour the temperature of the pellet has reached equilibrium

and substituting 4, 5 and 6 in equation 3

whence

Dividing though by 1-e

$$\frac{\partial}{\partial t} = \frac{\partial}{\partial t} + \frac{\partial}$$

Using all the results shown in figure 3.10 equation 11 was solved by corrolating

and n = 0.26 (14) Substituting this value of n in equation 2 for

$$\theta = 90 \cdot \theta_{0}$$

100
-0.26 t
(15)

whence

Cont'd.

In the case of silicon carbide the rate of heating will be faster since :

- 1. Pellets are slightly smaller.
- 2. Surface emilisivity of silicon carbide is higher than that of white alumina.
- 3. The thermal diffusity is about three times greater.

Therefore,

4. THERMODYNAMICS OF SILICON CARBIDE OXIDATION.

4.1 The Nature of the Problem.

The system under consideration is the oxidation of silicon carbide in air. It, therefore, contains the four elements, oxygen, nitrogen, silicon and carbon. It is assumed that nitrides do not form but silicon carbide, during heating, reacts with oxygen to form at least one oxide. Since both component elements of silicon carbide form two oxides a comprehensive treatment of the system must include the following :

1.	SiC		
2.	0 2 N 2		
4.	Si0 2		
5.	SiO	Table	4.1
6.	S1		
7	C0 2		
8.	CO		
9.	C		

9 elements and compounds.

The aim in thermodynamics is to determine the con ditions of equilibrium. In table 4.1, eight reactive components are listed and it can be shown that these lead to the

Cont'd.

- 39 -

- 40 -

following reactions - table 4.2.

the second se	בייני בייני איז איז איז איז איז איז איז איז איז אי
Reaction or Reaction Type	No. of Reactions
Silicon carbide formation	1
Silicon carbide oxidation by oxygen	8
Reactions involving silicon and	
oxygen only	4.
Reactions involving carbon and	
oxygen only	lų.
Redox reactions involving oxygen,	
silicon and carbon	9
Silicon carbide oxidation by oxide	14
	Total 40

Table 4.2

4.2 Assumptions.

To make the problem tractable some simplifications are necessary. Already it has been assumed that nitrogen is inert and this reduces the number of equilibria to be considered, but those outlined above are not all independent and in fact only five are needed to completely define the thermodynamics of the system. In table 4.1, five compounds are listed and the formation of these will be used as basic equations from which all others are derived. These reactions together with their standard free energies (AG^o) are given Cont'd.
in table 4.3.

FIGURE	4.3	The	free	energy	of	formation	of	the	principal
		CONT	onent	ts					

Si + C 🛹 SiC	& C [°]	1	-12780+1.71	 (1)
251+ 0 🛹 2510	AG	11	-46280-40.21	 (2)
Si + 0 que Si0	AG	=	-209680+42.3T	 (3)
20 + 0 = 200	Ac	N.	-53400-41.8T	 (4)
$C + 0 \neq C0$	AG	=	-94200-0.2T	 (5)

Although kinetic factors such as diffusion of air between the grains, may affect the approach to the equilibrium state, the systems examined are assumed to be closed in which equilibrium is attained.

Three other assumptions made in this discussion are as follows :

- I. Gases behave ideally.
- Each solid component exists as a separate phase exhibiting only negligible solubility of other components.

3. The system is at unit atmosphere pressure.

4.3 Method.

The second assumption necessitates restrictions since all the condensed phases cannot coexist under equilibrium conditions - for example, silicon and carbon react to form silicon carbide - therefore some restrictions must be made

and the method employed is to consider a number of condensed phase combinations. Each combination is then examined in the temperature range 0°C to 2000°C in 100° increments using thermodynamic and stoichiometric relations, and the results are given as tables 4.5 to 4.11.

The first stage in the analysis is to establish a formula for calculating the equilibrium partial pressure of one of the components in the gas phase (CO, CO, SiO and O). This proved to be the most difficult part because some of the equations are extremely complex and required iterative methods for solution with the aid of a digital computer. The partial pressure of the remaining components in the gas phase are then readily calculated including the partial pressure of nitrogen which is generally calculated by difference. These results are given in tables 4.5 to 4.9.

After composition of the gas phase has been established the quantities of the condensed phases that participate in the oxidation are calculated together with the amount of atmospheric oxygen used. These quantities are expressed as moles per mole of equilibrium gas phase in table 4.5 to 4.9 and further summarised in table 4.10. In this summary condensed phases are specified as being either reactants or products as functions of temperature.

Cont'd.

- 42 -

Using the calculated values of partial pressures of the gas phase components, the systems are then re-examined by considering the hypothetical state in which all the solid phases are present. This necessitates the assignment of non-unit activities to those phases originally excluded. These activity data are used to ascertain the stability of the system using the forgoing argument: if the activity is less than one the escaping tendency or chemical potential is less than the pure phase and therefore the system is stable, although if the phase was introduced into the system (physically) it would react with it; if the listed activity is greater then one the converse is true and the system may be said to be supersaturated with the excluded phase.

At high temperatures in the four phase systems it was found that the solution is only possible at pressures above one atmosphere. It follows that because practical firing of silicon carbide wheels is normally performed at about one atmosphere pressure the system is unstable and therefore oxidation will proceed until stability is attained by elimination of one of the condensed phases.

In table 4.11 the activity data and system pressure data are summarised using the above arguments, when three states are specified :

 If the system shows supersaturation the relevant phases are shown. Contid.

- 43 -

- 2. If no supersaturation is evident and if equilibrium is reached at unit atmosphere pressure the system is said to be "stable".
- 3. If the system attains equilibrium only at elevated pressures the system is said to be "unstable".

The first system to be analysed is the simple two phase system containing silicon carbide and gas only table 4.5. The results of this analysis suggest supersaturation with silicon and silica at low temperatures and therefore these components are introduced separately, and together - tables 4.6, 4.7 and 4.8. It is also apparent that carbon is stable over part of the silicon carbide/silica/gas system temperature range and therefore carbon is introduced in table 4.9. Thus five systems in all are considered and in the forgoing subsections they are referred to by Roman numerals as follows :

- I. silicon carbide/gas,
- II. silicon carbide/silica/gas,
- III. silicon carbide/silicon/gas,
- IV. silicon carbide/silicon/silics/gas,
- V. silicon carbide/silica/carbon/gas.

Throughout the calculations the following symbols (table 4.4) are used.

Cont'd.

- 44 -

Table 4.4

Symbol	Function
р	partial pressure
а	activity
n	number of moles
N	Fractional molar yield per
	mole of equilibrium gas
	phase (reactants are
A SUCCESSION	treated as negative products)
∆G°	standard free energy
T	absolute temperature (K)
K	Equilibrium constant at
C	temperature I.

N and n are also subscripted by the chemical symbols and the letters m, u, w, x, y, z, are used to denote number of moles in some of the stoichiometric equations to simplify retation.

4.4. System I - Silicon Carbide/Gas.

This equation is the summation of equations, 1, 2, 4 and 5 and thermodynamically it may be resolved into an initial Cont'd. dissociation of silicon carbide (equation 1) followed by oxidation of the elements to form a mixture of volatile oxides (equations 2, 4 and 5). Nitrogen has been omitted for simplicity but it should strictly occur/both sides of equation 6.

46 -

The method adopted for finding the conditions of this equilibrium, consists of developing an equation containing the partial pressures of the reactive constituents of the gas phase, reducing the degrees of freedom with thermodynamic and stoichiometric restrictions, solving for one of the partial pressures and then by substituting back into previous equations finding all the equilibrium pressures.

If n moles of oxygen are available for the oxidation of silicon carbide, then for conservation of oxygen in a closed system -

 $n = n + \frac{1}{2}n + \frac{1}{2}n + n$ (7) O2(R) SiO CO CO2

where n = number of moles of unreacted oxygen O2(R)

> n = " silicon monoxide = x SiO

n = " carbon dioxide = y CO2 : n = " carbon monoxide = z

CO

Assuming air to contain 80% nitrogen and 20% oxygen the number of moles of nitrogen, n , will be given by -

 $n_{N2} = 4n_{M2} + 4n_{M2} + 2n_{M2} + 2n_{M2} \dots (8)$ $N_{N2} = 02(n)_{M2} + 02(n$

wit from the ideal gas assumption equation 8 may be rewritten:

$$P_{N2} = {}^{h}p_{CO2} + {}^{2}p_{CO} + {}^{2}p_{S10} + {}^{h}p_{O2(R)} \dots (9)$$
there p = partial pressure.
The total pressure of the system p is given by

$$P_{TOT} = P_{N2} + P_{O2(R)} + P_{CO2} + P_{CO} + P_{S10} \dots (10)$$
therefore from equations 9 and 10

$$P_{TOT} = 5P_{O2(R)} + 5P_{CO2} + 3P_{CO} + 3P_{S10} \dots (11)$$
but $P_{TOT} = 1 \dots (12)$
therefore

$$5P_{O2(R)} + 5P_{CO2} + 3P_{CO} + 3P_{S10} = 1 \dots (13)$$
Silicon carbide contains equiatomic proportions of
silicon end carbon hence

$$n_{S10} = n_{CO2} + n_{CO} \dots (14)$$
or $P_{S10} = P_{CO2} + P_{CO} \dots (15)$
substituting in equation 13

$$5P_{O2(R)} + 8P_{CO2} + 6P_{CO} = 1 \dots (16)$$
Equation 16 can now be solved using equilibrium constants
to relate $P_{O2(Q)}P_{CO2}$ and P_{CO} , derived from the basic equations
1 to 5.
Cont'd.

- 47 -

b

Eliminating the elements oxygen, carbon and silicon from equations 1, 2, 4 and 5 yields SiC + 2CO \rightarrow SiO + 3CO $\triangle G^{\circ} = 4^{\circ}$... (17)

whence $K_{T}(17)$, the equilibrium constant, is given by

$$K_{T(17)} = \frac{p_{S10}, p_{C0}}{p^2 3}$$
(18)

substituting p from equation 15 and rearranging SiO

$$K_{T(17)} = p = p = p = 0 \dots (19)$$

Equation 19 is a quadratic in p for which the positive root is

$$P_{CO2} = \frac{3}{co} + \sqrt{\frac{6}{p} + \frac{4K}{r(17)}} + \frac{4}{co} + \frac{4}$$

The value of K can be derived from the standard free f(17)

energy, AG, of equation 17 thus -

$$K = -\Delta G^{2} RT = -49290/T + 42.325 \dots (21)$$

T(17) e e

To complete the solution of equation 16, p can be eliminated 02(A) as follows :

from eqations 4 and 5

$$2C0 + 0 = 2C0 \ \Delta G = -1.35000 + 41.4T \dots (22)$$

2 2

whence .

$$K (22) = p = e$$

$$T = \frac{C02}{2}$$

$$p = p$$

$$C0 = 02(R)$$

$$Cont'd.$$

The summation of equations 16, 20 and 23 reduces to :

$$_{4}^{5p}$$
 CO K (22) (p +1)+8p K (2p +1)
T CO CO T(17) CO
 $_{-p}^{2}$ (5K K (2p) (2p +1)
CO T(17) CO
 $_{-p}^{2}$ (5K K (2p) (2p +1)
CO T(17) CO
T(17) CO
T(17) CO
T(17) T (22) CO T (17) T (22)

+12p -2) +36)+12p -1 = 0 (24)

Equation 24 cannot be solved analytically, therefore an iterative method must be used. An Elliott 803 computer was programmed to solve the equation by such a method over the temperature range 0 to 2000 C and the results are given in table 4.5. The details of the programme are given in section 2 but the general method was as follows: . a value for p was assumed and p was calculated by substitution into equation 20. These values for p and p were inserted into equation 23 to find p and then equation 16 used to find the resulting atmospheric pressure. If this pressure was less than one, p was doubled and the procedure repeated until the equilibrium atmospheric pressure exceeded one. The result of these operations determines a range in which the correct value of p must lie, viz: between the last two values calculated, repeated bisection of this range was performed until the possible error was insignificant.

(N) and the number of moles of initial (or atmospheric) SiC Cont'd oxygen (N) involved in the reaction are given. These O2(I) quantities are defined as the number of moles produced per mole of equilibrium gas phase. It should be noted therefore that reactants are treated as negative products.

For the conservation of silicon :

$$N + N + p + N = 0 \dots (25)$$

sic sic2 $\frac{si0}{p}$
TOT

but in this section the yields of silice and silicon monoxide are assumed zero thus equation 25 reduces to

$$N = p / p$$
(26)
Sic Sio TOT

Similarly,

Combining equations 9 and 27

$$N_{02(I)} = -p_{N2}/4p_{TOT}$$
 (28)

To complete the analysis of the two phase system it remains only to calculate the activities, or escaping tendencies of the excluded phases, viz: carbon, silicon and silica. This is achieved using the relationship that exists between the equilibrium constant and the standard free energy of a reaction. Calculation is made simpler if reactions involving only one condensed phase are used.

From equations 4 and 5 :

whence

$$= \frac{p_{CO}^2}{p_{CO2}} = 20533/T - 20.94$$
(31)

From equation 2 :

9

 $K_{T(2)} = p_{Si0}^2 / (p_a^2) = e^{\frac{23292}{T+20.24}} ... (32)$

whence $a = \frac{p_{510}}{p^2} e^{-11646/T - 10.12}$ (33)

From equations 2 and 3 :

$$2Si0 + 0 \rightarrow 2Si0 \qquad \Delta G^{\circ} = -373080 + 124.8T \dots (34)$$

 $2 \qquad 2$
therefore $K_{T(34)} = a^{2} / (p^{2} p) = e^{\Delta G^{\circ}/RT} \dots (35)$
 $T(34) \qquad Si02 \qquad Si0 \qquad 02$
whence $a_{Si02} = p_{Si0} \qquad p^{\frac{1}{2}} = e^{9388/T-31.4} \dots (36)$

4.5 System II - SiC/SiO /Gas.

In table 4.5 it can be seen that the exclusion of silica from the products of oxidation leads to very high equilibrium activities for silica at low temperature; therefore at these temperatures silica would be expected to form. In this subsection the general equation

will be considered. This equation is similar to equation 6 except that silicon forms both its oxides. A similar treatment will be followed for equation 37 as for equation 6 although different equilibria and stoichiometry are pertinent.

For n moles of oxygen equation 7 now reads ;

$$n = n + n + n + \frac{1}{2}n + \frac{1}$$

whence

$$n = 4n = 4n + 2n + 4n + 2n \dots (39)$$

N2 S102 S10 C02 C0

However, equation 39 cannot be converted to a partial pressure equation since it contains n , but from the SiO2' stoichiometry of silicon carbide

substituting for n in equation 39 yields S102

whence

$$p = 4p - 2p + 8p + 6p \dots (42)$$

N2 O2(R) S10 CO2 CO

and

$$p = 5p - p + 9p + 7p \dots (43)$$

TOT 02(R) S10 C02 C0

Equation 43 contains 4 unknowns (p = 1) and therefore TOT a further three equations are required for its solution.

53. ~

These may be obtained as follows.

From equations 1, 3 and 5:

$$SiC + 20 \rightarrow Si0 + C0 \land G = -291100 + 40.4T ... (44)$$

 $2 \qquad 2 \qquad 2$

From equations 1, 3 and 4:

$$Sic + \frac{3}{20} \rightarrow Si0 + CO \ AG = -223600 + 19.7T \dots$$
 (46)

whence

$$K_{T(46)} = p / p^{3/2} = e^{112530/T - 9.912}$$
(47)
T(46) CO 02

From equations 2 and 3 :

whence

主言

$$K_{T(48)} = p p = e -93880/T+31.4$$
 (49)
T(48) 02 510

Substituting p p and p in equation 43 and equating p to one yields : TOT

$$\frac{2}{M_{T(44)}} + \frac{2}{02} + \frac{3^2}{T(46)} + \frac{5p}{02} - \frac{1}{T(48)} + \frac{1}{02} = 1 \dots (50)$$

If equation 50 is multiplied by p it can be seen that
it is a fifth order polynomial in p. It is impossible to
olve a fifth order polynomial analytically and therefore
equation 50 was solved iteratively in a similar manner to that

Cont'd.

cf 52

used in the previous section for the two phase system. The details of the programme are given in section 2. However, it was found during the early stages of development that the solution could yield negative values of p at high temperatures and therefore iteration was modified to find the lowest value of p consistent with a minimum value of one O2 for p and a minimum value of zero for p. The results TOT of this calculation are shown in table 4.6.

In table 4.6 the molar yields of silica are included. These was calculated as follows for the conservation of oxygen, using the same conventions as in section 4.4.

 $N + N + N + N + N + \frac{1}{5}N + \frac{1}{5}N = 0 \dots (51)$ 02(1) 02(R) 5102 C02 C0 510

whence

N = -N - (p + p + to to prove the since N cannot be converted to a pressure quotient since O2(I) the initial oxygen does not appear in the equilibrium state. However, N can be eliminated from equation 51 using O2(I) equation 28 thus :

N = (¹/_{N2} - ^p/_{O2(R)} - ^p/_{CO2} - ¹/_{S10})/^p/_{TOT} .. (53) SiO2 N2 O2(R) CO2 CO SiO TOT .. (53) The other values in columns 8 to 11 in table 4.6 were calculated in exactly the same manner as before except that N is not zero and must be included in the calculation of SiO2 N - equations 25 and 26. SiC Cont'd.

- 54 -

From table 4.5 it can be seen that in the absence of silica, activity of carbon is low over the whole temperature range and silicon is stable at low temperatures. Table 4.6 shows that the introduction of silica (which is always present in vitreous grinding wheels) renders carbon stable at low temperature and silicon stable at very high temperatures. In the next three sections therefore the systems containing

- 1. Silicon
- 2. Silicon and silica
- 3. Carbon and silica

will be examined.

4.6 System III - Silicon/Silicon Carbide/Gas.

The reaction to be considered is

mSiC + n0 wSi + xSiO + yCO + zCO (54) 2 in which silicon is only partially oxidised to SiO.

The arguments that applied to the two phase system apply here as far as equation 13 viz :

$$5p_{02(R)} + 5p_{02(R)} + 3p_{02(R)} + 3p_{02(R)} + 3p_{02(R)} = 1$$
(13)

though it is not possible to apply the restriction

$$n = n + n$$

 $si0 \quad C02 \quad C0$ (14)

and therefore the restriction

will be used to solve equation 13.

From equations 1 and 5 :

$$sic + 0 \rightarrow si + c0 \ \Delta G^{\circ} = -81420 - 1.91^{\circ} \dots (56)$$

whence

$$K_{T(56)} = \frac{p_{C02}}{p_{02}} = e$$

From equations 1 and 4 :

$$2S1C + 0 \rightarrow 2CO + S1 \ \Delta G = -27840 - 45.2T \dots (58)$$

whence

$$K_{T(58)} = p / p = e$$
 (59)
$$T(58) = c 0 02 = e$$

From equation 2 :

Substituting the above in equation 13 to eliminate p , CO2

p and p yields CO SiO

$$5(1+K)_{1}^{p} + 3(K^{\frac{1}{2}} + K^{\frac{1}{2}})_{02}^{p} - 1 = 0 \dots (61)$$

T(56) 02 T(58) T(2) 02

a quadratic in p of which the only positive root is 02

$$p_{02}^{\frac{1}{2}} = \frac{-3(K_{T(58)}^{\frac{1}{2}} + K_{T(2)}^{\frac{1}{2}}) + \left[9(K_{T(58)}^{\frac{1}{2}} + K_{T(2)}^{\frac{1}{2}})^{2} + 20(1+K_{T(56)})\right]^{\frac{1}{2}}.62}{10(1+K_{T(56)})}$$

Values of p were calculated over the temperature range 0 to 2000 C using equation 62 and then using equations 57, 59 and 60 values of p , p and p were calculated: CO2' CO SiO

the results are shown in table 4.7.

In table 4.7 the molar yield of silicon is given; this was calculated as follows. From the stoichiometry of silicon carbide

but in this section

$$N = 0 \qquad \text{occosecord} \quad (64)$$

therefore

Eliminating N using equation 53 and assuming ideal SiO2 gases equation 65 reduces to

 $N = (2p_{CO2} + 3/2p_{CO} + p_{O2(R)} - \frac{1}{2}p_{N2} - \frac{1}{2}p_{Si0})/p_{TOT} ... (66)$

Other values in table 4.7 were calculated as in the previous section except that the value of N from equation 66 Si must be substituted into equation 26 to calculate N SiC

4.7 System IV - Silicon/Silicon Carbide/Silica/Gas.

The equation to be considered is the sum of equations 6, 37 and 54, viz:

cannot be used but the restrictions

and

are available and these reduce the complexity of the algebra. The restriction

(70)

........

is now superfluous. This latter point will render the solution at unit atmosphere pressure impossible if the sum of reacting gases is greater than one, therefore the procedure will be to calculate p I from the equation TOT

$$p = p + p + p + p + p_{02(R)}$$
 (69)

then if

$$p_{TOT} \approx 1$$

$$p_{N2} = 1 - p_{TOT}$$

and

p = 1 TOT

otherwise

and

$$p_{TOT} = p_{TOT}$$
 (71)
Cont'd.

The equilibrium partial pressure of
$$P_{CO2}$$
, P_{CO} , P_{S10} and
 $P_{C2(R)}$ can be calculated as follows :
From equations 2 and 3
 $\frac{1}{2}$ 510 $_{2}$ + $\frac{1}{2}$ 510 Δ G[°] = 81700-41.25T (72)
whence
 $K_{T(72)} = p_{S10} = e^{-41117/T+20.777}$ (73)
From equation 3
 $K_{T(72)} = 1/p_{02} = e^{1.05526/T-21.29}$ (74)
whence
 $-105526/T+21.29$ (74)
 $T_{T(3)} = 1/p_{02} = e^{1.05526/T+21.29}$ (75)
From equations 1, 3 and 5
S1C + S10 \rightarrow C0 + 2S1 Δ G[°] = 128260-44.2T ... (76)
whence
 $K_{T(76)} = p_{C2} = e^{-64550/T+22.22}$ (77)
From equations 1, 3 and 4
S1C + $\frac{1}{2}$ S10 \rightarrow C0 + $1\frac{1}{2}$ S2 Δ G[°] = 90920-43.75T ... (78)
whence
 $K_{T(78)} = p_{C0} = e^{-45732/T+22.02}$ (79)
The values of P_{C02} , p_{C0} , p_{S10} and p_{O2} Were calculated over
the range 0 to 2000 C and the results are shown in table 6.8
Cont'd.

p and p were calculated from equations 71 and 72 and the remaining quantities were calculated as described in the previous subsections.

$$\begin{array}{rcl} \underline{+,8} & \underline{\text{system V}} = \underline{\text{Silica/Silicon Carbide/Carbon/GAS}}{\text{The equation for consideration here is :}} \\ & \underline{\text{mSiC} + n0} \xrightarrow{\rightarrow} \sqrt{\text{SiO}} + \sqrt{\text{SiO} + \sqrt{\text{CO}}} + \sqrt{\text{CO} + zC} & \dots & (80) \\ & 2 & 2 & 2 & 2 \\ \end{array}$$
The equation differs from equations 6, 37, 54 and 67 in that it contains carbon in elemental form; however, its treatment is identical to the previous case except that a = 1 & \dots & (81) \\ & and & a = 1 & \dots & (81) \\ & and & a = 1 & \dots & (55) \\ & but & a \neq 1 & \dots & (55) \\ & but & a \neq 1 & \dots & (82) \\ & & \text{Therefore from equations 1, 3 and 5 :} \\ & & \text{SiC} + \text{CO} \xrightarrow{\rightarrow} \sin_2 + 2C & \Delta G^\circ = -1027004 \pm 0.8T & \dots & (83) \\ & & \text{whence} & -51690/T \pm 20.53 \\ & & & p_{\text{CO2}} & T(83) \\ & & & \text{From equations 1, 3 and 4 :} \\ & & & & \frac{1}{2}\text{SiC} + \text{CO} \xrightarrow{\rightarrow} \frac{1}{2}\text{SiO} & + 3/2C & \Delta G^\circ = -71750 \pm 41.2T & \dots & (85) \\ & & & & & 2 & 2 \\ \end{array}

From equations 1, 2 and 3 :

 $\frac{1}{2}$ sic + $\frac{1}{2}$ sic + $\frac{1}{2}$ $\Delta G = 88090 - \frac{1}{2} \cdot 11 \cdot \cdot \cdot \cdot (87)$

whence

$$p_{si0} = K = e^{-44333/T+21.19}$$
 (88)
si0 T(87)

From equations 1 and 3

$$sic + 0 \rightarrow si0 + c \Delta c = -196900+40.6T \dots$$
 (89)

whence

The values of p p and p were calculated over O2(R), CO2 SiO the range O to 2000 C and the results are shown in table 4.9; p and p were calculated as before from equations 71 N2 and 72. The molar yield of carbon was calculated as follows:

but since

 $N = 0 \qquad (91)$ Si $N = N + N - N - N \qquad (92)$ C SiO2 SiO CO2 CO Comparison with equation 65 shows that $N = -N \qquad (92)$ C (NSI=0) SI (NC=0) (93)

TABLE 4.5 SHOWING EQUILIBRIUM CONDITIONS FOR SYSTEM 1. VIZ SIC/02/SIO/CO2/CO/N2

P(02.R)	P(CO2)	P(CO)	P(\$10)	P(N2)	P(TOT)	Т	N(SIC)	N(02.1)	A(C)	A(51)	A(\$102)
3.830-61	1.258-01	6.160-21	1.25@-01	0.750	1.00	0	-0,125	-0,187	1:13@-16	2.4204-06	0.0004-00
3.510-46	1.250-01	6.260-14	1.25@-01	0.750	1.00	100	-0,125	-0.188	2.04@-11	7.41@+03	0.000+00
2.408-37	1.25@-01	5.508-10	1.258-01	0.750	1.00	200	-0.125	-0.187	1.39@-08	2.080+02	2.23@+53
1.008-31	1.25@-01	2.36@-07	1.25@-01	0.750	1.00	300	-0,125	-0.187	1.31@-06	2.37@+01	1.300+41
8.960-28	1.250-01	1.670-05	1.25@-01	0.750	1.00	400	-0,125	-0.187	3.21@-05	5.13@+00	3.300+32
7.608-25	1.25@-01	3.930-04	1.25@-01	0.750	1.00	500	-0,125	-0.187	3.43@-04	1.66@+00	1.408+26
1.360-22	1-220-01	4.400-03	1.26@-01	0.748	1.00	600	-0,126	-0.187	2.108-03	7.008-01	1.71@+21
7.870-21	1.050-01	2.71@-02	1.32@-01	0.736	1.00	700	-0,132	-0,184	8.28@-03	3.79@-01	2.16@+17
1.68@-19	5.980-02	8.708-02	1.47@-01	0.707	1.00	800	-0.147	-0.177	2.080-02	2.798-01	1.380+14
1.320-18	1.840-02	1.428-01	1.61@-01	0.679	1.00	900	-0.161	-0,170	3.53@-02	2.75@-01	2.44@+11
5.368-18	4.328-03	1.618-01	1.65@-01	0,670	1.00	1000	-0, 165	-0.167	4.888-02	3.068-01	9.410+08
1.610-17	1.108-03	1.65@-01	1.66@-01	0.667	1.00	1100	-0. 166	-0.167	6.23@-02	3.46@-01	7.630+06
4.08@-17	3.29@-04	1.66@-01	1.67@01	0.667	1.00	1200	-0.167	-0.167	7.65@-02	3.87@-01	1.17@+05
9.140-17	1.140-04	1.67@-01	1.67@-01	0.667	1.00	1300	-0, 167	-0.167	9.15@-02	4.278-01	3.060+03
1.860-16	4.478-05	1.678-01	1.67@-01	0.667	1.00	1400	-0.167	-0.167	1.07@-01	4.67@-01	1.230+02
3.490-16	1.958-05	1.678-01	1.67@-01	0.667	1.00	1500	-0.167	-0.167	1.23@-01	5.05@-01	7-110+00
6.110-16	9.288-06	1:.67@-01	1.67@-01	0.667	1.00	1600	-0.167	-0.167	1.39@-01	5.41@-01	5-57@-01
1.010-15	4.768-06	1.67@-01	1.67@-01	0.667	1.00	1700	-0, 167	-0.167	1.55@-01	5.768-01	5.660-02
1.608-15	2.610-06	1.670-01	1.67@-01	0.667	1.00	1800	-0, 167	-0.167	1.72@-01	6.109-01	7.168-03
2.420-15	1.518-06	1.678-01	1.670-01	0.667	1:00	1900	-0.167	-0.167	1.888-01	6.428-01	1.109-03
3-53@-15	9.168-07	1.67@-01	1-67@-01	0.667	1.00	2000	-0, 167	-0.167	2.058-01	6.738-01	1.980-04

P = PARTIAL PRESSURE IN ATMOS. T = TEMPERATURE IN DEG.C. A = ACTIVITY OF SOLID PHASESN = MOLES OF REACTANT OR PRODUCT PER MOLE OF GAS PHASE (REACT. -VE 1 PROD. +VE) TABLE 4.6 SHOWING EQUILIBRIUM CONDITIONS FOR SYSTEM 11. VIZ SIC/02/SI02/SI0/C02/C0/N2

P(02.R)	P(C02)	P(CO)	P(510)	P(N2)	P(TOT)	т	N(SIC)	N(S102)	N(02.1)	A(C)	A(S1)
8.640-78	1.250+70	1.308459	0.009+00	&	&	0	-0,111	+0,111	-0,222	5.04@+71	0,000+00
8.640-78	4.140+07	1.320+11	7.278-58	&	ě.	100	-0,143	+0,143	-0,214	2.75@+29	2.75@-37
2.668-67	3-410-08	1.438-01	5-330-40	0:857	1.00	200	-0,143	+0,143	-0,214	3.44@+15	8.43@-22
2.808-55	1-260-07	1-438-01	5-748-31	0.857	1.00	300	-0,143	+0,143	-0,214	4.77@+11	6.520-17
7.860-47	3.158-07	1-43@-01	1.280-24	0.857	1.00	400	-0, 143	+0,143	-0,214	9.280+08	1.78@-13
1.448-40	6.228-07	1.430-01	6.518-20	0.857	1.00	500	-0,143	+0,143	-0.214	9.080+06	6.25@-11
9.680-36	1.058-06	1-430-01	2.768-16	0.857	1.00	600	-0,143	+0.143	-0,214	2.56@+05	5-75@-09
6.63@-32	1.598-06	1-430-01	2.108-13	0.857	1.00	700	-0.143	+0.143	-0,214	1.510+04	2.098-07
8.758-29	2.240-06	1.430-01	4.660-11	0.857	1.00	800	-0,143	+0.143	-0,214	1.509+03	3.87@-06
3.398-26	2.978-06	1.430-01	4.108-09	0.857	1.00	900	-0,143	+0.143	-0,214	2.228+02	4.37@-05
5.168-24	3-760-06	1-,430-01	1:79@-07	0.857	1.00	1000	-0, 143	+0.143	-0,214	4.42@+01	3-37@-04
3.778-22	4.600-06	1.438-01	4.508-06	0.857	1.00	1100	-0,143	+0.143	-0,214	1,120+01	1.938-03
1.548-20	5.480-06	1.438-01	7.318-05	0.857	1.00	1200	-0, 143	+0.143	-0,214	3.39@+00	8.73@-03
3-930-19	6.408-06	1-43@-01	8.320-04	0.856	1.00	1300	-0, 143	+0,142	-0,214	1.2004-00	3.26@-02
6.820-18	7-380-06	1-440-01	7.07@-03	0.849	1.00	1400	-0.144	+0,137	-0,212	4.83@-01	1-03@-01
8.788-17	8.758-06	1.509-01	4.678-02	0.804	1.00	15 00	-0, 150	+0,103	-0,201	2.209-01	2.828-01
9-420-16	1.228-05	1-770-01	2.410-01	0.582	1.00	1600	-0,177	-0,064	-0.145	1.19@-01	6-308-01
1.03@-14	2.808-05	3.07@-01	9-228-01	0.000	1.23	1700	-0,250	-0.500	+0,000	8.998-02	9.978-01
1-290-13	1.210-04	8.640-01	2.598+00	0,000	3.46	1800	-0,250	-0.500	+0,000	9.948-02	1-0664-00
1-280-12	4.58@-04	2.210+00	6.630+00	0,000	8.83	1900	-0.250	-0.500	+0.000	1-090-01	1.11@+00
1.030-11	1.540-03	5-200+00	1-560+01	0.000	20.8	2000	-0,250	-0.500	+0,000	1.180-01	1.160+00

P = PARTIAL PRESSURE IN ATMOS. T = TEMPERATURE IN DEG.C. A = ACTIVITY OF SOLID PHASES N = MOLES OF REACTANT OR PRODUCT PER MOLE OF GAS PHASE (REACT. -VE : PROD. +VE)

TABLE 4.7 SHOWING EQUILIBRIUM CONDITIONS FOR SYSTEM 111. VIZ SIC/02/SI0/SI/C02/C0/N2

P(02.R)	P(CO2)	P(CO)	P(\$10)	P(N2)	P(TOT)	Т	N(S1)	N(SIC)	N(02.1)	A(C)	A(\$102)
5.009-67	2.008-01	8.560-18	5-908-11	0.800	1.00	0	+0,200	-0.200	-0,200	1-36@-10	0.000+00
1.498-49	2.008-01	4.810-12	3.488-07	0,800	1-,00	100	+0.200	-0,200	-0,200	7.53@-08	0,009+00
1.828-39	2.008-01	1.008-08	5.230-05	0.800	1.00	200	+0.200	-0,200	-0,200	2.880-06	8.13@+48
6.69@-33	1.99@-01	1.450-06	1-,368-03	0.799	1.00	300	+0.198	-0.199	-0,200	3.098-05	3.67@+38
2.668-28	1.920-01	4.698-05	1.330-02	0.795	1.00	400	+0,179	-0.192	-0.199	1.64@-04	1.909+31
5-838-25	1.608-01	5-718-04	6.620-02	0.773	1.00	500	+0.094	-0,161	-0.193	5.65@-04	6.488425
1.408-22	8.860-02	3.130-03	1.830-01	0.726	1.00	600	-0.091	-0,092	-0,181	1.46@-03	2.510+21
5.15@-21	2,620-02	8.34@-03	2.810-01	0,684	1.00	700	-0,247	-0.035	-0, 171	3.12@-03	3-73@+17
5.808-20	5.820-03	1.430-02	3.098-01	0.671	1.00	800	-0,289	-0,020	-0, 168	5.780-03	1.710+14
3.710-19	1.440-03	2.07@-02	3-100-01	0.668	1.00	900	-0,288	-0.022	-0, 167	9.63@-03	2.508+11
1.710-18	4.258-04	2.788-02	3.058-01	0.667	1.00	1000	-0.277	-0, 028	-0.167	1.48@-02	9.809+08
6.16@-18	1.470-04	3.540-02	2.988-01	0.667	1-00	1100	-0,262	-0.036	-0.167	2.148-02	8.46@+06
1.858-17	5.828-05	4.340-02	2.908-01	0.667	1.00	1200	-0,246	-0.043	-0, 167	2.948-02	1-379+05
4.780-17	2.570-05	5-150-02	2.820-01	0.667	1.00	1300	-0,230	-0, 052	-0.167	3.880-02	3.73@+03
1.098-16	1.240-05	5-960-02	2.748-01	0.667	1.00	1400	-0,214	-0,060	-0.167	4.96@-02	1-550+02
2.258-16	6.410-06	6.778-02	2.668-01	0.667	1.00	1500	-0,198	-0,068	-0,167	6.160-02	9.11@+00
4.288-16	3.558-06	7.550-02	2.589-01	0.667	1.00	1600	-0,182	-0.076	-0,167	7.480-02	7.22@-01
7.588-16	2.078-06	8.310-02	2.508-01	0.667	1.00	1700	-0,167	-0, 083	-0, 167	8.908-02	7.340-02
1-268-15	1.278-06	9.040-02	2.430-01	0.667	1.00	1800	-0, 153	-0.090	-0,167	1.048-01	9-278-03
2.008-15	8.078-07	9.748-02	2.360-01	0.667	1.00	1900	-0.139	-0.097	-0.167	1.208-01	1.418-03
3.038-15	5.338-07	1-040-01	2.298-01	0.667	1.00	2000	-0,125	-0.104	-0.167	1.37@-01	2.528-04

P = PARTIAL PRESSURE IN ATMOS. T = TEMPERATURE IN DEG.C. A = ACTIVITY OF SOLID PHASESN = MOLES OF REACTANT OR PRODUCT PER MOLE OF GAS PHASE (REACT. -VE : PROD. +VE) TABLE 4.8 SHOWING EQUILIBRIUM CONDITIONS FOR SYSTEM IV. VIZ SIC/02/SI02/SI0/SI/CO2/CO/N2

P(02.R)	P(C02)	P(CO)	P(\$10)	P(N2)	P(TOT)	т	N(S1)	N(SIC)	N(S102)	N(02.1)	A(C)
0.000+00	0.000+00	5.809-64	4.04@-57	1.000	1.00	0	-0.250	+0.000	+0.250	-0.250	0.0004-00
0.000+00	3.12@~66	1.909-44	1-39@-39	1.000	1.00	100	-0,250	+0,000	+0.250	-0.250	0.003+00
0.0004-00	2.428-50	3.49@-33	1.83@-29	1.000	1.00	200	-0.250	+0,000	+0.250	-0.250	2:900-06
1.82@-71	5-34@-40	7.519-26	7.110-23	1.000	1.00	300	-0.250	+0,000	+0.250	-0,250	3.118-05
1.408-59	9.94@-33	1.07@-20	3.04@-18	1.000	1.00	400	-0.250	+0,000	+0.250	-0.250	1.65@-04
9.008-51	2.43@-27	7.078-17	8.23@-15	1.000	1.00	500	-0.250	+0,000	+0.250	-0.250	5:680-04
5-568-44	3-470-23	6.22@-14	3.64@-12	1.000	1.00	600	-0.250	+0,000	+0.250	-0,250	1.47@-03
1.380-38	6.930-20	1.360-11	4.61@-10	1.000	1.00	700	-0,250	+0,000	+0,250	-0.250	3-14@-03
3-39@-34	3.360-17	1:09@-09	2.378-08	1.000	1.00	800	-0.250	+0.000	+0.250	-0,250	5.810-03
1.480-30	5-670-15	4.13@-08	6-208-07	1.000	1.00	900	-0.250	-0,000	+0,250	-0,250	9.698-03
1-748-27	4.280-13	8.850-07	9.740-06	1.000	1.00	1000	-0,250	-0,000	+0.250	-0.250	1.49@-02
7.298-25	1.720-11	1.210-05	1.02@-04	1.000	1.00	1100	-0,250	-0,000	+0.250	-0,250	2.160-02
1-350-22	4.180-10	1-17@-04	7.820-04	0.999	1.00	1200	-0,250	-0,000	+0.249	-0,250	2.96@-02
1.280-20	6.780-09	8.408-04	4.61@-03	0.995	1-,00	1300	-0.250	-0,001	+0.246	-0,249	3.910-02
7.05@-19	7-88@-08	4.780-03	2.208-02	0.973	1.00	1400	-0.247	-0.005	+0,200	-0.243	4.998-02
2.47@-17	6.940-07	2.24@-02	8.809-02	0.890	1.00	1500	-0.233	-0.022	+0,167	-0,222	6.209-02
5-938-16	4.850-06	8.878-02	3.030-01	0.608	1.00	1600	-0,171	-0.089	-0.044	-0.152	7.53@-02
1.030-14	2.788-05	3.068-01	9.23@-01	0,000	1.23	1700	-0,002	-0.249	-0.500	+0.000	8.968-02
1.368-13	1.35@-04	9.36@-01	2.520+00	0,000	3.46	1800	+0,041	-0,271	-0.500	+0,000	1.058-01
1.428-12	5.65@-04	2.798+00	6.290+00	0.000	8.87	1900	+0.083	-0-292	-0.500	+0.000	1.21@-01
1.208-11	2.098-03	6.53@+00	1.44@+01	0,000	21.0	2000	+0-123	-0,311	-0.500	+0,000	1-380-01

 $\label{eq:partial pressure in atmos.} T = TEMPERATURE IN DEG_C. A = ACTIVITY OF SOLID PHASES N = MOLES OF REACTANT OR PRODUCT PER MOLE OF GAS PHASE (REACT. -VE : PROD. +VE)$

TABLE 4.9 SHOWING EQUILIBRIUM CONDIDIONS FOR SYSTEM V. VIZ SIC/02/SI02/SI0/C02/CO/C/N2

P(02.R)	P(CO2)	P(CO)	P(\$10)	P(N2)	P(TOT)	т	N(C)	N(SIC)	N(5102)	N(02.1)	A(S1)
0.008+00	4.94@-74	3.640-49	4.710-62	1.000	1.00	0	+0.250	-0.250	+0,250	-0,250	0.000+00
0.000+00	5.460-52	9.15@-34	3.810-43	1.000	1.00	100	+0.250	-0,250	+0.250	-0,250	-4.89@+16
0.0004-00	2.89@-39	7.098-25	3.128-32	1.000	1.00	200	+0.250	-0,250	+0.250	-0.250	-2.95@+30
5.860-67	5.53@-31	4.33@-19	3.960-25	1.000	1.00	300	+0.250	-0.250	+0.250	-0.250	3.11@-05
8.47@-56	3.660-25	5.050-15.	0.900-20	1.000	1.00	400	+0.250	-0,250	+0,250	-0,250	1.65@-04
1.59@-47	7.55@-21	5.220-12	1.96@-16	1.000	1.00	500	+0.250	-0.250	+0.250	-0,250	5.64@-04
0.78@-41	1.60@-17	1.10@-09	1.409-13	1.000	1.00	600	+0.250	-0.250	+0.250	-0,250	1.47@-03
4.400-36	7.03@-15	7.730-08	2.580-11	1.000	1.00	700	+0.250	-0.250	+0.250	-0.250	3.14@-03
5.83@-32	9-93@-13	2.460-06	1.800-09	1.000	1.00	800	+0,250	-0.250	+0,250	-0,250	5.81@-03
1.53@-28	6.030-11	4:33@-05	6.110-08	1.000	1.00	900	+0.250	-0.250	+0.250	-0,250	9.69@-03
1.17@-25	1.92@-09	4.860-04	1.190-06	1.000	1.00	1000	+0.249	-0,250	+0.250	-0,250	1.49@-02
3.38@-23	3.708-08	3.830-03	1.508-05	0.996	1.00	1100	+0.243	-0.247	+0.247	-0.249	2.15@-02
4.54@-21	4.76@-07	2.298-02	1.35@-04	0.977	1.00	1200	+0,210	-0,233	+0.233	-0.244	2,960-02
3.27@-19	4.43@-06	1.09@-01	9.120-04	0.890	1.00	1300	+0,060	-0.169	+0.168	-0,223	3.91@-02
1.41@-17	3.16@-05	4.28@-01	4.910-03	0.567	1.00	1400	-0.498	+0,070	-0.075	-0,142	4.99@-02
3.99@-16	1.810-04	1.450+00	2.19@-02	0.000	1.47	1500	-1.470	+0.485	-0.500	+0,000	6.208-02
7.88@-15	8.560-04	4.29@+00	8.320-02	0.000	4.08	1600	-1.462	+0.481	-0.500	+0,000	7.53@-02
1.15@-13	3.47@-03	1.14@+01	2.76@-01	0,000	11.7	1700	-1.453	+0.477	-0.500	+0,000	8.960-02
1.309-12	1.23@-02	2.760+01	8.179-01	0,000	28.4	1800	-1.443	+0.471	-0.500	+0,000	1.05@-01
1.17@-11	3:86@-02	6.150+01	2.190+00	0,000	63.7	1900	-1.432	+0.466	-0.500	+0,000	1.21@-01
8.71@-11	1.109-01	1.280+02	5.360+00	0.000	133	2000	-1.420	+0.460	-0,500	+0,000	1.380-01

P = PARTIAL PRESSURE IN ATMOS. T = TEMPERATURE IN DEG.C. A = ACTIVITY OF SOLID PHASES N = MOLES OF REACTANT OR PRODUCT PER MOLE OF GAS PHASE (REACT. -VE : PROD. +VE)

4.9 Detailed Discussion of Thermodynamic Tables.

The object of this section was to find the equilibrium conditions for silicon carbide oxidation. The chemistry is complex but in section 4.2 it was reduced thermodynamically to five reactions. Assumptions were made to render the problem tractable and in particular it was assumed that the system was closed. Analysis proceeded by studying various phase combinations of increasing complexity and the results are shown in tables 4.5 to 4.9. In the following discussion three aspects are considered; partial pressures; stoichiometry, ie: the condensed phases of the system are introduced and activities, where those phases excluded from the definition of the system, are considered. From the general survey, speculations regarding the most likely equilibrium states can be made.

In all cases the oxygen content of the equilibrium phase, as indicated by its partial pressure, is very small, being less than 10 % though it increases with rise in temperature. These factors are consistent with the instability of silicon carbide discussed in section 1 and the exothermic nature of silicon carbide oxidation.

The equilibrium partial pressure characteristics of carbon monoxide and carbon dioxide vary considerably between systems. In the two phase system (system I) table 4.5,

carbon dioxide is predominant at low temperatures changing over to carbon monoxide at high temperatures the change over point being ca 800°C. This phenomenon is related to the thermochemistry of carbon. The enthalpy of oxidation to carbon dioxide is more negative than to carbon monoxide and therefore at low temperatures, when the entropy contribution to free energy is small, carbon dioxide is the most stable. However, the oxidation of carbon by oxygen to the lower oxide involves a large volume expansion since one molecule of oxygen forms two of carbon monoxide, thus:

Consequently the entropy of the system increases resulting in a large free energy reduction at high temperature, so that at higher temperatures the monoxide becomes stable in the case of pure carbon oxidised by oxygen at one atmosphere pressure the change over occurs at ca 723 C.

The introduction of silice, table 4.6 (ie: system II) changes the reactions completely. Below 200°C the iterative solution has not converged correctly owing to a computer store size limitation but at 200°C and above it can be seen that carbon monoxide is the chief oxide and that the partial pressure of carbon dioxide rises slightly with temperature. The reason for the low carbon dioxide partial pressure is presumably a result of the high stability (very negative free

Cont'd.

- 63 -

energy of formation) of silica. The partial pressure of oxygen is therefore low promoting the formation of carbon monoxide. However, this very negative free energy is largely due to its enthalpy of formation - the reaction is extremely exothermic - and therefore as the temperature is raised the oxide tends to dissociate producing a rapidly rising oxygen partial pressure and this increases the tendency to form carbon dioxide.

The introduction of silicon into the systems does not change the basic pattern described above although actual partial pressures are changed. In the case of the system IX (ie: silicon carbide/silica) the effect of silicon, table 4.8, reduces the partial pressures of all the gaseous products. It can be seen from inspection of table 4.8 that this is due largely to the instability of silicon which is oxidised preferentially to silica thus yielding an atmosphere which is almost 100% nitrogen at low temperatures. The introduction of carbon has a similar affect to silicon particularly in the silicon carbide/silica system, though for a different reason. In the case of carbon table 4.9 (system V) it tends to be liberated at lower temperatures by partial oxidation of silicon carbide to silics and carbon; therefore an atmosphere very rich in nitrogen tends to develop especially at low temperatures.

Cont 1d.

- 64 -

Silicon monoxide is a major product in the two phase system (silicon carbide/gas). This follows from the definition of the system which only permits oxidation to the volatile oxides. However, increasing the complexity of the system tends to reduce the partial pressure of the silicon monoxide as discussed above in relation to the effects of silicon and carbon. The inclusion of silica effects a reduction in silicon monoxide yield because of its greater stability (ie: its more negative free energy of formation).

The behaviour of nitrogen, at lower temperatures is the reverse of silicon monoxide: in the sense that increasing the complexity of the system tends to increase its equilibrium partial pressure. In the simplest two phase system only gaseous products of oxidation can accrue while in the more complex systems solid products are possible, eg: silica and elemental carbon, so that in extreme cases nitrogen may be virtually the only gas present in the gas phase. However, silica can also be a reactant at high temperatures becoming an oxidising agent. When this happens solution at unit atmosphere may be impossible, as the system is defined, and it becomes necessary to raise the system pressure to a level at which solution is possible, this has the effect of excluding nitrogen from the system.

All the data for the gaseous components has been given as partial pressures; however, this does not permit Cont'd.

- 65 -

stoichiometric conclusions to be drawn. To do this the data must be converted to a molar q uantity and this can be achieved by dividing each partial pressure by the total pressure of the system (usually 1) to give mole fraction, ie: moles per mole of equilibrium gas phase. Also required is the participation of the condensed phases and this is given in tables 4.5 to 4.9 commencing with column 8 where the units are already as mole fraction (moles per mole of equilibrium gas phase). However, condensed components may be reactants or products and this is signified by sign as stated previously. Atmospheric oxygen is treated as the condensed phases; it cannot be assigned a pressure since it does not exist in the gas phase and it participates as a reactant. In table 4.10 a summary is given showing for each system how oxygen and the condensed phases react over the total temperature range. In this table the components are specified as being either reactants or products.

For the simple two phase system I, table 4.5, it can be seen that at > 0 C :

 $\frac{1}{6}\sin(2) + \frac{3}{16} = 0 + \frac{3}{2}\sin(2) + \frac{3}{6}\cos(2) + \frac{3}{2}\cos(2) +$

ignoring the trace concentrations of oxygen and carbon monoxide and omitting nitrogen which was assumed to be inert in 4.1.

Cont'd.

- 66 -

TABLE 4.10

				5	Y i	5 T .	Ci Di Antonio Tari	-A		TU	TY I Y					
ature.	sic	02	Sic	\$10	102	Sic	SJ.	02	Sic	Si	S10	02	510	51.Q	G	
0	Carried States and	annand		annin ann					7							
100									1							
200							TOO		V,							
300							RODI		Y,							
4.00							Ai		Y,	a Canvin (m						
500							reference series		1							
000									1							
700									1							
800									K							
900									K					1		
1000								F .:					ANT	E	TOI	
1100	LANT	CART	LANT	TOD	LANI	CANT	TANT	LA NJ	V.	LAND	107	FANT	SACT	RODA	RODE	
1200	EAC.	EACT	EAC.	RODI	EAC	EAC	EAC	EAC	4	EAC	RODI	EAC	RI	E	A	
1300	R	R	X	A	R	pel -	R	R		X	D.	E	-	1	ana	
1400																
1600										1	-					
1700									ANT			7	1	E	T	
1800				THAN	1				TACT	-	E	and a	TOCH	TAN	TAN	
1900				EACT	1				RI	EDD0	CTA	/	PROL	REAC	REAL	
				R	1					FRO	REA	-	1			

Equation (94) can be rationalised by removing the fractions, when

$$2 \operatorname{sic} + 30 \xrightarrow{2} 2 \operatorname{sio} + 2 \operatorname{co} 2 2$$

Similarly at 2000 C

$$\frac{1}{6}$$
 $\frac{1}{6}$ $\frac{1}{2}$ $\frac{1}{6}$ $\frac{1}$

whence

$$\operatorname{SiC} + 0 \Longrightarrow \operatorname{SiO} + \operatorname{CO} \qquad \cdots \qquad \cdots \qquad \cdots \qquad \cdots \qquad \cdots \qquad \cdots \qquad (97)$$

Equations 95 and 97 define the stoichiometry of pure silicon carbide oxidation at low and high temperatures respectively. However, there must be a change over point and from inspection of columns 8 and 9, table 4.5, it can be seen that there is a transition range from about 700°C to 900°C where both reactions are important.

Applying the same procedure to system II (table 4.6) at 200°C (below 200°C iteration is incomplete) it can be seen that

 $2 \text{ sic } + 30 \xrightarrow{2 \text{ sio}} 2 \text{ sio} + 2 \text{ co} \qquad \dots (98)$

ie: when silica is introduced into the system it forms in preference to silicon monoxide. Equation 98 applies up to about 1400°C though above 1400°C the silica yield decreases and silicon monoxide becomes a significant product; at 1500°C about 30% of the silicon from the carbide is oxidised to the lower form. At 1600°C silica becomes an oxidising agent and at 1700°C it replaces air completely so that the Cont'd.

67 -

stoichiometry becomes

The introduction of silicon rather than silica (ie: system III table 4.7) results in a more complex system of reactions. Up to and including 300°C the principal equation is

ie: silicon now replaces the silicon monoxide of equation 95. However, above 300°C the yield of silicon decreases rapidly, silicon being partially oxidised to the monoxide. At 600°C and above silicon ceases to be a product and the following three equations have to be considered.

SiC + 0 -> SiO + CO			 •	• •	• •	• •	0	0	0	•	0 1	0 0	2 10	. 6	0	(97)
251C + 30 → 2510 + 2C0 2	2	•			• •	• •		0	•		• •				0	(95)
28i + 0 -> 28i0			 •						0	•		9 1			0	(101)

ie: (95) low temperature oxidation of silicon carbide (97) high temperature oxidation of silicon carbide; (101) silicon oxidation - all in the absence of silica. At 600°C equations 95 and 101 combine to produce

and the contribution made by equation 97 is negligible. At 700 C equation 97 starts to gain significance at 800 C it exceeds the contribution made by equation 95 when the Cont'd. contribution of equation (101) reaches a maximum. As the temperature is raised the same trends continue so that at 2000 C the stoichiometry is approaching

this equation can be resolved into

 $\operatorname{SiC} + 0 \longrightarrow \operatorname{SiO} + \operatorname{CO}$ (97)

ie: the chemistry of this system approaches that of the two phase system I with the oxidation of silicon superimposed.

When silica and silicon are both included in the system we find that silicon is preferentailly oxidised to silica up to 1400 °C by the equation

Above 1400°C the oxidation of silicon carbide becomes significant though at 1600°C the proportion of silicon oxidised to silicon carbide oxidised is still 2:1, when the gross stoichiometry is

58iC + 68i0 + 108i + 70 → 21 8i0 + 500 (105) 2 2

this equation can be resolved into

 $sic + 0 \rightarrow co + sio \qquad \dots \qquad (97)$ $sic + 2sio \rightarrow 3sio + co \qquad \dots \qquad (99)$ $2si + 0 \rightarrow 2sio \qquad \dots \qquad (101)$ cont'd.

thus the reaction described by equation 105 is similar to that of system II except that silicon oxidation, to its monoxide is superimposed. At 1700°C the contribution made by equation 101 becomes negligible and equation 97 drops out completely, ie: the system becomes virtually identical to system II. Above 1700°C silicon becomes a product and the stoichiometry can then be resolved into equation 99 (ie: system II) together with the equation

Carbon like silica can be a reactant or a product tending to be a product at low temperatures and a reactant at high temperatures. System V, ie: silicon carbide/silica/ carbon/gas, is given in table 4.9 where it can be seen that up to 1200 C silicon carbide is partially oxidised yielding silica and carbon according to the equation

However, at 1200 C the gas phase starts to become significant. Initially the gas phase is carbon monoxide and at 1300 C the equation for oxidation is

which can be resolved into
thus the formation of carbon is reduced, and the stoichiometry approaches that of the silicon carbide/silica system presumably the two systems become identical when the carbon activity in system II is one. At 1400°C equation 107 is reversed with the result that both silica and carbon become reactants yielding the equation

As the temperature is raised silica becomes the only source of oxygen and at 1500 C the equation becomes

As the temperature is further raised silicon monoxide formation starts to become significant according to the equation

 $28C + 10510 \rightarrow 951C + 510 + 19C0 \dots (112)$

The third, and final, aspect of this discussion concerns the activity data presented in the terminating columns of tables 4.5 to 4.9. As already pointed out the significant factor is relative size of these figures compared to unity and as explained in section 4.3, a summary is given in table 4.13 Cont'd.

TABLE 4.11

	System No.								
Temp.	I	TI	III	IV	V				
0 100 200 300 400 500 600 700 800 900 1000 1100 1200 1300	Si & SiO2	C	810 ₂	Stable	Stable				
1500		Stable							
1600		weine 1772 alloca villate 1873		1011 -10 100 -100 40 400	-				
1800									
1900	Stable		Stable						
2000		Si							

= Unstable i.e silica becomes the sole agent & equilibrium cannot be achieved at unit atmosphere pressure.

Table showing supersaturation in restricted systems

The starting point in this thermodynamic section 4 has been the consideration of the oxidation of pure silicon carbide. In table 4.11 it can be seen that up to 500 C this system is supersaturated with both silicon and silica.

If silicon is included as a condensed phase table 4.11 shows that this system, ie: system II, is still supersaturated with silica and remains so up to 1500°C; this leads to the prediction of system IV (see section 4.3). Table 4.11 shows that system IV shows no supersaturation although at 1700°C and above, equilibrium is only obtained above unit atmosphere pressure. However, in system III, at and above 1600°C, supersaturation with silica ceases. Therefore thermodynamically for systems III and IV no distinction of maximum likelihood can be made in this temperature range.

Above 500 C system I still exhibits supersaturation with silica though when silica is added to give system II carbon supersaturation is evident up to 1300 C. This fact predicts system V to be more likely up to 1300 C (in the absence of silicon). However, in system V non-unit pressure is required for equilibrium at and above 1400 C. Over the range 1400 C to 1500 C system I is still supersaturated with silica though system II is unsaturated; therefore in the absence of silicon and carbon the most likely system in this temperature range is system II.

Contid.

- 72 -

At and above 1600 C system I ceases to show supersaturation and in fact only system II shows any supersaturation above this temperature and this commences at 1800 C; therefore in the range 1600 C to 1700 C no thermodynamic prediction of maximum likelihood can be made and from 1800 C all that can be stated is that system II is unlikely. However, it must be noted that in this temperature range all those systems containing silice do not necessarily reach equilibrium at unit atmosphere pressure.

- 73 -

These facts concerning the probability of various phase combinations are summarised in table 4.12 where the expected phase combinations are shown as functions of temparature and original composition.

In section 4.3 it was shown that not all combinations of condensed phases are possible. However, one possible combination that has not been considered is that containing the condensed phases silicon carbide and carbon only. This combination did not arise during the theoretical derivation of tables 4.5 to 4.9 and it was not introduced as an additional case since the combination is not found in practice. Newertheless for the sake of completeness this system can be included in table 4.12 where it is referred to as system VI. From table 4.0 (system V) it can be seen that in the presence of silicon carbide and carbon, silica is a product of

TABLE 4.12

	ORIGINAL COMPOSITION								
Temp.	V	VI	I	II	IV	III			
0	an an ann an								
100									
200									
300									
400						3.78			
500	·G .:								
700	DI	; 5102							
800									
900	S1C+S10-+S1								
1000		Non your	-2,22						
1100 1200									
1300									
1400			-	0:0.					
1500		Sec.		SIU; SIU;		for the second s			
1600				2					
1700	-	SiC;	Sid			SiC;			
1800		0		Si					
1900									
2000	-			-					

= Equilibrium cannot be obtained at unit atmosphere pressure.

Table showing the effect of temperature on the stability of components.

oxidation up to 1300°C. From table 4.11 the combination silicon carbide/silica/carbon is most likely in the absence of silicon. Therefore, even if initially excluded silica will tend to be a product. Above 1300°C it can be assumed absent since it only enters system V as a reactant.

4.10 Conclusions.

The thermochemistry of silicon carbide oxidation can be explained by the relative stabilities of the various oxides, ie: by their free energies of formation. At low temperatures the free energies of formation fall in the sequence

$$\Delta G^{\circ} \underset{2}{\overset{<}{\overset{<}{\overset{}}}} \Delta G^{\circ} \underset{CO}{\overset{<}{\overset{}}} \Delta G^{\circ} \underset{CO}{\overset{<}{\overset{}}} \Delta G^{\circ} \underset{SiO}{\overset{<}{\overset{}}} \Delta G^{\circ} \underset{SiO}{\overset{<}} \Delta G^{\circ} \underset{SiO}{\overset{}} \Delta G^{\circ} \underset{SiO}{\overset{<}{\overset{}}} \Delta G^{\circ} \underset{SiO}{\overset{}} \Delta G^{\circ} \overset{SiO} \underset{SiO}{\overset{}} \Delta G^{\circ} \overset{SiO}{\overset{}} \Delta G^{\circ} \overset{SiO} \overset{SiO}{\overset{}} \Delta G^{\circ} \overset{SiO}{\overset{} } \Delta G^{\circ} \overset{SiO}{\overset{}} \overset{SiO}{\overset{}} \Delta G^{\circ} \overset{SiO}{\overset{} } \Delta G^{\circ} \overset{SiO}{\overset{} } \Delta G^{\circ} \overset{SiO}{\overset{} } \overset{SiO}{\overset{} } \Delta G^{\circ} \overset{SiO}{\overset{} } \overset{}$$

so that the most stable oxide is silica and the least silicon monoxide.

Cont'd.

was 1725 and

In system II silica, because of its greater stability, replaces silicon monoxide but in addition it tends to take the oxygen in preference to carbon so that oxidation proceeds by the equation

 $2S1C + 30 \longrightarrow 2S10 + 2C0 \qquad (98)$

In system III an analogous mechanism operates. Here the very negative free energy of formation of CO takes 2 the oxygen preferentially so that the oxidation equation is

 $\frac{\text{SiC} + 0}{2} \frac{\text{Si} + C0}{2}$

Leaving aside system IV for the moment, system V is seen to be a further extrapolation of system II in which all the oxygen now goes to the silica, thus:

Equation 107 shows that silica is a much more stable oxide than any other (at low temperatures) and forms preferentially even breaking more silicon carbide bonds. In system IV essentially the same principle operates by a different mechanism, ie: the preferential oxidation of silicon which again avoids the oxidation of carbon, thus :

When the temperature is raised the relative stabilities may change because of the different entropies of reaction due largely to the different volume changes associated with

the formation reactions of the oxides. The contribution to free energy, made by entropy, in the case of silicon monoxide approximates to that of carbon monoxide since the two reactions of formation, viz:

(4)

are similar, both involving the volume increase associated with one mole of gas. Therefore, when the temperature is raised the relative free energies of formation remain the same though both become more negative. (The expansion is associated with a positive entropy change). However, the silica formation reaction

involves a volume decrease, necessitating a decrease in entropy, so that raising the temperature reduces the stability of this oxide. The free energy of formation, and hence stability, of carbon dioxide is affected little by temperature since the formation reaction

involves no major volume change. The overall result is that at high temperatures (ie: at 2000 C) the free energies

 $\Delta G^{\circ}_{CO} < \Delta G^{\circ}_{SiO} < \Delta G^{\circ}_{CO} < \Delta G^{\circ}_{CO} < 0 \dots (114)$ $2 \qquad 2 \qquad 2 \qquad Cont'd.$

It may be noted that silica is still more stable than carbon dioxide although their free energies of formation will be closer.

The relative change in stability between carbon dioxide and carbon monoxide produces a movement to the monoxide in systems I and III, with temperature rise, and in both cases the oxidation equation becomes

However, in system III the situation is made slightly more complex by the inclusion of silicon. As the temperature is raised the silicon monoxide yield increases rapidly and at 600°C it replaces silicon completely when silicon becomes a reactant. The first effect can be explained solely by the increase in stability of silicon monoxide though the second requires a little more consideration. In section 4.9 the thermochemistry of system III, at 600°C, was resolved into system I, ie:

with the oxidation of silicon to silicon monoxide superimposed. However, an alternative method would have been to superimpose the equation

3S1 + CO -> 2S1O + SiC (115) 2 Now at 500 C and below the oxidation can be resolved into Cont'd.

- 77 -

95 and the reverse of 116 viz:

- 78 -

and in fact equation 100 (the 0 C equation for system III) is the simple addition of 95 to 116, as written. It can now be seen that the transfer of silicon from the product side to the reactant side occurs because the increase in stability of silicon monoxide outweighs the stability of carbon dioxide to the extent that it is able to reverse equation 116.

Systems II, IV and V can be explained using similar techniques except here the relevant oxide stabilities as those of silicon monoxide and carbon monoxide over silica.

In system II, equation 98 can be resolved into

and 3Si0 + CO -> Si0 + SiC (118)

Equation 118 shows that it is the high stability of silica over the other oxides, at low temperature, that renders the formation of silica a more likely product of oxidation and this is shown right across table 4.12. However, as the temperature is raised equation 118 is opposed by the changes in oxide stability and at 1600 °C it is reversed so that silica becomes a reactant in system II and no longer a likely product of oxidation of pure silicon carbide. At Cont'd. 1700 C the progress of equation 118 in the reverse direction, viz:

$$sic + 2 sio \rightarrow 3 sio + co \dots (99)$$

produces such a high yield of silicon monoxide and carbon monoxide that equilibrium can only be reached at elevated pressures and the contribution made by atmospheric oxygen to the oxidation process is eliminated.

In system IV the low temperature equation

can be resolved into

ie: system II together with the simultaneous replacement of silicon carbide by equation 119 driven by the high stability of SiO over CO. However, as the temperature is 2 raised equation 119 becomes less likely and consequently some silicon carbide is oxidised. Similarly system IV can be resolved over the entire temperature range in this way and consequently its thermochemistry is basically that of system II. In table 4.12, for example, it can be seen that at 1600°C silica also ceases to be a likely product of oxidation of silicon carbide in the presence of silicon. At 1800°C

- 80 -

equation 119 is reversed to give

so that system IV is similar to system II with equation 106 superimposed. It also means that silicon becomes a likely product of silicon carbide oxidation in the presence of silica at high temperature.

System V can be treated in the same way resolving equation 107 into

As in the case of equations 118 and 119, equation 120 is favoured by the high stability of silica and it is this equation which is responsible for the likelihood of carbon formation, at low temperatures, in the absence of silicon. Again, as the temperature is raised equation 120 is opposed and at 1300°C equations 98 and 120 occur in the ratio 4:1 to give

so that carbon becomes a reactant. At 1400°C the promotion of equation 110, by the relative increase in stability of Cont'd. silicon monoxide and carbon dioxide over silica, causes silica and silicon carbide to change sides of the equation and in the presence of carbon therefore silica becomes an unlikely product of silicon carbide oxidation. At 1500°C (as in system II and IV at 1700°C) the inverted equation suppresses oxidation by atmospheric oxygen with the concomitant elevated equilibrium total pressure. However, the equation

is also favoured by the oxide stability changes and therefore silicon monoxide becomes a significant product of oxidation in system V as the temperature is further raised. Thus, in general, silica and carbon are favoured by low temperatures due to the very negative free energy of formation of silica, and silicon and silicon monoxide are favoured by high temperatures, due to relatively low stability of silica, which favours such reactions as equations 106 and 111 although elevated pressure may be necessary.

5. DISCUSSION.

~ 82

In section 3 basic studies were reported on the system silicon carbide/bond/binder while in section 4 a figorous analysis of the thermodynamics of silicon carbide oxidation was made. In this section the results of the experimentation and thermodynamic investigation are discussed and the sequence adopted approximates to that in which experiments were performed although the main object has been to elucidate mechanisms. Thus the discussion may be divided into the two main aspects of the research viz: thermogravimetric examination of oxidation and visual examination of oxidation. The former is discussed in section 5.1 through to section 5.5 and the latter in section 5.6 to section 5.8.

The first stage in the research was to consider the pyrolysis of pure binders and the results of these experiments are analysed in section 5.1. In section 5.2 and section 5.3 the effects of morphology and dispersion are examined where the results of dilation experiments are also examined. The effect of bond on binder removal is first introduced in section 5.4 where tests performed at 1000 C are examined together with compressive strength test results. In section 5.5 it is shown that oxidation of the abrasive, although it did not contribute significantly to the previous

pyrolysis curves, did exhibit interesting characteristics.

The second aspect of the work is based on visual examination and two types of pellet were used, viz: alumina and silicon carbide. The alumina tests are discussed first where the effect of bond composition in particular is examined and from this a criterion of carbon entrapment by the bond is evolved. In this subsection the beneficial effects of controlled heating rates is demonstrated and the ill effects of poor temperature distribution. In the next section (section 5.7) a thorough investigation of the kinetics of carbon removal from the silicon carbide pellets is made and the reason for the existence of three zones in the soft defect is derived. The results of the previous subsections are discussed in the light of these later tests where the effect of decomposition, oxidation, fusion and wetting are related to porosity, permeability, time and temperature. In section 5.8 the thermodynamics of carbon burn-out are discussed and here both the silicon carbide pellet results and the thermodynamic conclusions are used. In particular a mechanism for the formation of the shiny black core by the precipitation of carbon from partially oxidised silicon carbide is developed and it is shown how the closed system, originally conceived in section 4, can be realised by restricted ingress of air (or CO) into the structure. Cont'd.

83 -

-

5.1 The Pyrolysis of Pure Binders.

The results of pyrolysis of pure binders are shown in figures 3.1.1 to 3.1.4.

84 -

The pyrolysis curve for starch (figure 3.1.1) shows that the weight decreased with temperature rise. However, the curve is not a smooth one but passes through five stages. The first is obviously due to drying and it can be seen that the rate of drving was not constant but increased rapidly with temperature. It started immediately above room temperature and it was completed by approximately 120 C. and as indicated in section 3 an excess of 20 C above 100 C is probably due to a temperature head necessary for heat transfer. In the manufacturing process this stage will normally be completed at a separate drying stage, and therefore not directly significant during firing. The second stage of pyrolysis is a constant weight period. bounded by the maximum temperature for drying and the minimum for decomposition. During the third period the rate of change in weight with temperature reached a maximum. At about 260 C the rate of weight loss abruptly changed to a lower value and weight loss continued, with slight fluctuation, until the final stage, which is essentially constant weight, was reached. Figure 5.1 illustrates a typical cycle.



Temperature >

figures 3.1.2 to 3.1.4 where the same analysis can be applied to dextrin, glucose and a sample of dried glucose. In the case of dextrin (figure 3.1.2) stage II was particularly well defined though for glucose (figure 3.1.3) it was a mere inflexion. Obviously stage I is absent in the dried glucose curve and from the same curve (figure 3.1.4) it can be seen that stage III had no definite starting temperature which is consistent with the poorly defined stage II in figure 3.1.3. For starch a smooth curve was obtained but dextrin and glucose further subdivide, although this effect is more marked in the dried glucose test. In all cases stage I terminated at ca 120°C and stage III at ca 260°C even though the dried glucose sample was heated at a very much faster rate (ca 300 C per hour instead of 50 C per hour). The termination temperature of stage IV was different for each binder. The glucose decomposition was completed at ca 430°C, followed by dextrin at ca 480°C and starch in excess of 500 C - it is difficult to quote a figure for starch since the weight decreases from ca 450 C to 600 C. The effect of rapid heating (in the case of dried glucose) was to raise the termination temperature ca 150 C due to heat transfer and kinetic factors.

Starch and dextrin are both solid binders and the weight decrease at stage I was 9 - 9.5% (ca 9% for starch Cont'd.

85

and 9.5% for dextrin), however, glucose, which is a inquire, decreased in weight by on 15%. Two important points are to be noted here: firstly, drying may have an important effect on porosity and pore structure and consequently this stage may have important indirect effects on subsequent binder removal: secondly, a large reduction in binder at this stage means a smaller mass to be removed at stages III and IV for equal starting weights.

Stage II is essentially time wasted in the kiln during manufacture. Furthermore, it may be disadvantageous, tending to promote migration of binder towards the centre of a wheel leading to the formation of a relatively dense carbonaceous "plug" difficult to burn cut. During the firing process a temperature gradient in the wheel is essential for heat transfer. However, this will mean that the centre of a wheel may be at stage II although the surrounding area contains binder undergoing thermal decomposition. It seems likely that this combination will result in some of the products of pyrolysis escaping towards the "cold centre" of the wheel, particularly heavy tar-like fractions which can condense readily. The mechanism is illustrated in figure 5.2.

Stages III and IV represent the bulk of the weight loss, due to pyrolysis, and their sum is in fact equal to the dry fraction of the sample (see figure 3.1.4). Considering the binders in the sequence, starch, dextrin,



The possible effect of stage 2 on binder distribution

glucose and dried glucose, stage III constituted ca 50%, 30%, 37% and 40% of the total weight loss of the binders while stage IV ca 40%, 60%, 50% and 60% of the total weight losses.

Stage III is probably due mainly to dehydration which in contrast to drying involves the removal of hydrogen and oxygen bound chemically into the carbohydrate molecule. The process is called caramellisation and it produces a residue rich in carbon. Consequently the ratio of stage III to stage IV, is related to the degree of carbonisation. Comparison between starch and dextrin curves (figures 3.1.1 and 3.1.2) shows that starch is carbonised more at stage III than dextrin. If it is assumed that only dehydration occurs at this stage and that these binders, in the dry state, contain 28.6% carbon (from the formula C_H_O_) then at the end of stage III the starch residue will contain 65% carbon while the dextrin will contain only 43% carbon. From figure 3.1.3 it may appear at first sight that glucose was intermediate between these two. However, as already pointed out stage III commences more readily with glucose and this can be explained by its different structure. Unlike either starch or dextrin, glucose is not polymerised and the molecular formula is thus C H 0, (ie: n(C H 0).H 0 6 12 6 6 10 5 2

where n=1) and since the extra molecule of water is very loosely bonded, dehydration started at a lower temperature. Cont'd.

- 87 -

Assuming that the initial carbon content was 25%, it follows that at the end of stage III the glucose residue contained 44% carbon based on figure 3.1.3 and 41% based on figure 3.1.4, io: glucose was virtually the same as dextrin in this respect with an average value of 42.5%.

The chemistry of stage IV is probably complex involving at least two types of reaction: further thermal decomposition plus final oxidation. In all cases the slope changed during this stage tending to be steeper at higher temperatures. With increase in temperature reaction rates generally become faster and this may explain most slope changes, and for starch there is no evidence to suggest any other mechanism. However, with the other binders the slopes changed more abruptly (over narrower temperature ranges).

For dextrin in particular, and to some extent dried glucose, the slope decreased above 350°C before increasing again. This suggests that above 350°C a reaction (or series of reactions) approached completion. It appears therefore that the increase in reaction rate with temperature rise over stage IV is due, at least in part, to a change in mechanism, probably from thermal decomposition to oxidation and a further consideration supports this. When carbohydrates are thermally decomposed the solid residue tends to become progressively more carbonised (or caramellised) and therefore it would be expected that two trends will Cont'd.

- 88 -

develop consecutively (though perhaps overlapping in a central temperature range). Firstly, the gaseous products probably become more dense (less saturated) as the reaction proceeds reflecting the increasing complexity of the binder; secondly, at some stage the evolution of gaseous products will start to decrease as the residue becomes deficient in hydrogen and oxygen atoms. Under the conditions of testing the binder was placed at the bottom of a crucible while in the firing of a wheel the binder (or rather binder residue) will tend to be found at the centre of the wheel, is at the centre of a porous mass. In either case it seems likely that the evolution of heavy gases will protect the residue, partly by preventing access of oxygen to the residue and partly by limiting heat transfer. However, the rate of replenishment of the gas must keep pace with its oxidation or dispersion, due to convection or diffusion, and it is unlikely that this will be delayed indefinitely by merely increasing the density of the gas. Eventually a point must be reached where the layer becomes unstable and ceases to protect the underlying residue. Up to this point the rate of weight decrease will be controlled by the rate of evolution of the gaseous products which in turn will be controlled by temperature and by the composition of the residue. Beyond this point however, the rate of weight loss will depend upon when the rate of oxidation controlled by Cont'd.

- 89 -

temperature and availability of oxygen.

In both test and the manufacturing process the temperature increases with time, tending to accelerate oxidation. However, the change with time in the availability of oxygen may be different: under test conditions increased convection in the furnace will tend to bring more oxygen in contact with the binder residue, but in the wheel, convection and diffusion may be impeded by fusion of the bond if it reduces permeability.

- 90 -

As already indicated starch is caramellised to a greater extent at stage III (65%) and consequently the concentration of hydrogen and oxygen atoms necessary to form volatile decomposition products, and hence a protective layer, will be less. Oxidation will start sooner and the main change in slope will be due to a steadily increasing oxidation rate with temperature rise.

Stage V represents the completion of pyrolysis. It may be noted that in no case is the recorded weight zero the lowest recording was obtained with dextrin (figure 3.1.2) and the highest with glucose (figures 3.1.3 and 3.1.4). It is difficult to analyse this effect, although two factors are probably involved. Water evaporation (due to drying) between weighing out and testing - in each case the initial weight recorded by the thermobalance was assumed to be 100% so that any discrepancy in the initial weight would appear



at the end of the test - and convection currents, as shown in figure 5.3, may have impinged on the crucible base to give a high weight recording.

5.2 Binder Morphology.

Figures 3.1.5 and 3.1.6 show the results of two further tests performed on dextrin and glucose. These tests differ from the previous in one respect only: the samples used were larger, is 1 gram instead of $\frac{1}{2}$ gram. The two curves show stage III terminated by an apparent weight increase.

To investigate these anomalous weight recordings, tests were made on dextrin and glucose but stopped towards the end of stage III. The results are shown in figures 3.2.1 and 3.2.2. It can be seen that both binders expanded to an enormous extent and it is concluded that the effect was caused by the binders protruding above the crucible top and touching the furnace wall. In the case of starch no anomalous effects were found and when a sample was taken to 260°C and removed from the furnace the residue was still compacted in the base of the crucible, similar to dextrin at 220°C.

The large expansions appear to be associated with glucose and dextrin which have smaller molecules. Furthermore, the glucose molecule is much smaller than dextrin and figures 3.2.1 and 3.2.2 show that while dextrin was still

Cont'd.

··· 91 ···

compact in the base of the crucible at 220 C glucose had expanded to the rim of the crucible, and at 240 C the glucose sample had still expanded most.

A possible explanation of this phenomenon is that dehydration occurs by condensation polymerisation rather than by the formation of anhydrohexoses from individual saccharide units in the case of the smaller mono- and aligo-saccharide structures of glucose and dextrin but not in the case of the already highly polymerised macro-molecule of starch. The highly viscous material produced is then dilated by water vapour.

In the firing process this phenomenon may affect binder burn-out. It would seem self evident that for burn-out to proceed the wheel structure must remain permeable, ie the pore structure must not consist of discrete voids but long interconnected channels. This structure may be developed adequately by the proceeding operations of mixing, pressing and drying but at the firing stage become blocked if a viscous material expands to fill the open pores. Thus mass transfer will be restricted to that part of the wheel from which binder has already been removed and consequently binder removal will be limited to the progression of a narrow front at the junction of these two zones, instead of being distributed over a much wider band, as would be expected when porosity is interconnected and mass transfer unimpeded. Cont 'da

- 92 -



FIGURE 5.4.1. showing unimpeded mass transfer.

FIGURE 5.4.2. Pores blocked by viscous decomposition products.

A simple model of the basic stages of binder removal

FIGURE 5.4.5.

Binder free structure.

Structure

partly oxidised and decomposed containing binder.



Binder before decomposition atarts.

3.5

P



111

11





This is illustrated in figures 5.4.1 and 5.4.2. In both these figures, three structures are shown, viz: those containing original binder, partially decomposed (or oxidised) binder and no binder, all having simultaneous existence. However, in practice this need not occur although the above theory requires the existence of at least two structures (or stages) in figure 5.4.2 but not in figure 5.4.1, where for thin sections particularly, the oxidation zone may extend over the whole section: this is illustrated in figure 5.4.3.

One beneficial effect of dilation follows from its effect on the morphology of the carbonaceous binder residue. If the binders are placed in decreasing order of frothing tendency, they are :

Glucose - Dextrin - Starch

the same sequence that would be obtained if placed in order of increasing stage IV termination temperature (discussed in section 5.1). It is likely that frothing has a dispersing effect on the final residue and consequently the binder which undergoes the least frothing forms the most dense residue, while the binder that undergoes the most frothing forms the most finely divided residue. Subsequent oxidation of the finely divided residue will tend to proceed more rapidly while the most dense residue will oxidise more slowly. The effect of this in a wheel is difficult Cont'd.

- 93 -

to estimate but it will probably be smaller than indicated by the tests made here since in a wheel the binders are already in a fairly finely divided state and the additional dispersing effect of frothing may be diminished. However, an attempt is made below to examine the general effect of dispersion.

5.3 Dispersion.

The general shape of the curves discussed in section 5.1 involving five stages appears to be reflected in figures 3.3.1 to 3.3.3 which depict the tests involving mixtures of binders with silicon carbide; although the change points are in some cases less well defined.

In these later tests stage I involved water added to facilitate mixing, and from the results on dextrin (figure 3.3.2) where a variety of compositions were tested, it would appear that the upper temperature limit to stage I is dependent upon water content. Furthermore, in each case there appeared to be more superheat required and this is presumably related to the extra mass to be heated to temperature. The weight percentages are in each case based on the initial weight of binder used. For dextrin the weight loss at the end of stage I agreed well with that obtained for the pure binder.

- 94 -

For starch, stage II was more clearly defined as a separate stage though three different weight values were observed. There did not appear to be any relationship between composition and weight, and the differences were probably due to experimental error. If this is assumed, and a "correction" applied, so that each stage II is brought to ca 90%, it can be seen that the starting weights for the 2% and 5% water mixings would be separated such that the 5% starts at higher weight percentage than the 2%; this is consistent with the proposal that water is lost by evaporation prior to weighing since a smaller error would be expected on the larger weight. Again, for glucose there appeared to be discrepancies between the pure binder tests and the leter test which suggests that glucose has a dry weight of 75% of original weight (instead of 85%).

In the case of glucose, the discrepancy observed above may have another explanation. The nucleation of glucose from solution is very difficult and on drying it tends to form a very viscous syrup which becomes quite resilient. The result is that drying is impeded by the formation of a "dry skin". It is possible that in the pure binder tests the formation of such a layer led to a premature termination of stage I, while in the present experiment, because the glucose was spread over a very large surface area, it dried completely. This theory is consistent with other observations.

Cont'd.

- 95 -

In the dried binder tests (section 5.1), stage III commenced almost immediately on heating above room temperature and although the loose bond between the saccharide molecule and the extra elements of water may be important, some of the effect may have been due to protvacted drying. In figure 3.1.3 the poorly defined stage II may be explained similarly, and even though it is not easy to compare this test with figure 3,3.3, the inflection between stages I and III does appear to have approached closer to a zero decomposition rate in the latter.

The termination temperatures of stage II, and stage III for starch and dextrin, were slightly higher in the dispersed tests than in the pure binder tests which is consistent with the idea of an increase in temperature head.

At the end of stage IV, however, a different pattern emerges. As with pure binders starch required the highest temperature to complete burn-out, and glucose the lowest. However, the actual temperatures were lower and much closer together. These two observations tend to confirm the theory that dispersion favours oxidation. In the previous section, dispersion was important only as the result of previous decomposition characteristics, while here there is the additional effect of dispersion over the surface of the abrasive and it would appear that this has a bigger influence tending to diminish the contribution made by stage III.

Cont'd.

- 96 -

The effect on starch is particularly noticeable. In the pure binder tests the last stages of oxidation were very protracted while in figure 3.3.1 it is seen that the termination temperature of stage IV is no less definite for starch than for dextrin or glucose.

5.4 Binder Decomposition and Oxidation in the System Silicon Carbide: Bond: Binder.

So far pure binders have been considered and the effect of dispersion by admixture with abrasive. In this section the system is completed by the inclusion of bond. The first test, involving all three components, were performed on the thermobalance. They are shown in figures 3.4.1 and 3.4.2 where the results of tests made on pellets of 46 mesh silicon carbide together with 20% vitreous bond and 2% starch after compacting to ca 1 ton per square inch are shown.

To produce the curve in figure 3.4.1 programmed heating of 50°C per hour was used and the weight changes were similar to those obtained without bond present. However, stage I was less well defined and this suggests that the bond, which contains a high proportion of clay, tends to inhibit drying. Stage III commenced slightly earlier than in the binder/ abrasive tests and in fact the curve at this point is very Cont'd.

- 97 -

similar to that of pure binder. However, it is difficult to explain this in terms of experimental error - for example, as a zero error on the temperature scale - since bhe onset of stage IV was higher than in either the pure binder or the binder/abrasive tests, and in fact occurred above 300°C.

The high upper temperature to stage III may be explained partly as the result of slower rate of decomposition (dehydration) and partly by a larger amount of decomposition at this stage. The first effect may be related to the poor definition of stage I. Clay tends to adsorb water onto its surface, but the saccharide molecule is surrounded by hydrogen and hydroxyl groups and it is probable that these are also adsorbed. If this occurs, removal of these groups will be more difficult. The second effect may be due either to a chemical effect involving one of the bond constituents or to a higher order of dispersion: in the pure binder experiments, starch was tested as a coherent mass; in the subsequent binder/abrasive tests the binder was thinly spread over a large surface area, but in these later tests, the binder will also be dispersed by mixing with the bond as this was in the form of a very fine powder.

Stage IV, in common with previous tests involving starch, gave no evidence of a transition from thermal Cont'd.

- 98 -

decomposition to oxidation. However, one noticeable deviation does emerge: the end of stage IV was not reached even after 14 hours of test, by which time a temperature of 700°C had been attained - 200°C above the end of stage IV, shown in figure 3.3.1.

The second test (figure 3.4.2) showed the effect of isothermal firing at 1000 C and the curve shows mone of the characterisitics of the earlier programmed tests. When a pellet is plunged into a hot furnace the surface heats up rapidly producing a very steep temperature gradient, consequently, the burning out process proceeds from the surface inwards. It is suggested that under this condition all the stages occur simultaneously, at points along the radius, and the result is a "smoothed or averaged" curve.

One noticeable effect is that after about 1 minute the burn-out rate decreased rapidly and there are two possible explanations for this. The first is that the change in rate of weight loss corresponded to the transition at stage IV from decomposition to oxidation although fusion or partial fusion of the bond reduced permeability. Initially, binder removal occurs by decomposition, and it seems likely that permeability will have minimal effect on rate since any constraint imposed by low permeability will result in a build up of pressure which, if it does not disrupt the pellet or wheel, will force decomposition products towards the surface.

- 99 -
However, the oxidation stage requires diffusion to allow the transfer both of oxygen in and oxidation products out of the structure. Furthermore, the pressure must be atmospheric and consequently, permeability becomes a significant rate controlling factor. The second explanation is afforded by figure 3.8. In this test compressive strength is plotted against time, and although the results of these tests are extremely scattered, there was a minimum which occurred at approximately 1 minute. The initial decrease in strength was presumably due to binder decomposition and the increase to bond fusion. It has already been pointed out that burn-out will start at the surface, and it is therefore suggested that the rapid rate change in figure 3.4.2, and the minimum in figure 3.8 coincide with the complete removal of binder at and near the pellet surface. This is reflected in the compressive strength tests as it allows both fusion of the bond and wetting of the silicon carbide by the bond which then develop resilience on cooling; in figure 3.4.2, the same effect leads to entrapment of the carbonaceous residue located near to the pellet centre. These two theories are not necessarily mutually exclusive and both a change in thermochemistry and a change in surface structure may contribute to the observed effect. Nevertheless, despite the scatter between results, figure 3.4.2 does show that sub-Cont'd.

100 -

sequent burn-out is slow and that the time required for complete binder removal may run into hours rather than minutes, even though the temperature is at least double that required, under more favourable conditions (see figure 3.3.1).

It was felt, at this point, that it was not pertinent to the programme to continue producing more data of the type above and subsequent pellets were not weighed but sectioned to permit visual examination. Results are shown in figures 3.6.1 to 3.6.4 where it can be seen that both temperature and compacting pressure were varied.

5.5 Abrasive Oxidation Experiments.

The results of these tests are shown in figure 3.5.1 and 3.5.2, also two additional figures viz: 5.5 and 5.6 are deduced from these.

Three factors probably contribute to the apparent weight changes shown in these figures :

- 1. Convection
- 2. Oxidation of impurities or non-stoichiometric carbon.

3. Oxidation of silicon carbide to silica.

However, the weight changes are extremely small, being no larger than 0.1% and consequently any conclusions must be tentative. It is also apparent that any direct



FIGURE 5.5 The effect of firing temperature on the weight minima reached during isothermal firing



contribution that silicon carbide oxidation may have made in the binder pyrolysis tests was negligible.

In figure 3.5.1 the results are shown of programmed heating at 50 C/hour for 46 mesh silicon carbide. The curve labelled C46 was a retest using the same sample of abrasive. It is seen that during the initial test (labelled C46) a minimum occurred in the weight at ca 750 C. This may have been due to the oxidation of non-stoichiometric carbon or impurities. It was decided to investigate this phenomenon further and to do this samples of abrasive were isothermally fired at various temperatures on either side of the minimum. The results are shown in figure 3.5.2 where the same sequence was observed. However, the initial weight rise was about 17mgm in each case and virtually instantaneous - this must have been caused by convection produced by plunging a cold crucible and sample into a preheated furnace.

For the tests performed at 650 C and lower the apparent weight decrease can be divided into two stages separated by a constant weight portion. The first part was completed in each case within 4 minutes and it is assumed to be due entirely to the subsidence of convection, and therefore this has been taken as zero (see section 3.2). The second stage is again thought to be due either to impurity or carbon oxidation although the abrasive was not discologred. If

Cont'd.

- 102 -

non-stoichiometric carbon is assumed, it suggests that discolouration by carbon formation involves the formation of a separate phase, which is consistent with the report in section 1 of work by Erwin who shows that the appearance of silicon carbide after oxidation by air is different if previously discoloured.

The tests carried out at 750°C and higher did not show the same constant weight portion, but from the general trend of the lower temperature tests this is seen to be due to a more rapid entry into the second stage such that the two stages merge.

The results of retesting the 850 C sample shows the same pattern up to ca 4 minutes but then the weight increases to a steady state plateau. The weight increase may be due to further oxidation although it is difficult to see why a constant weight should be reached. Nevertheless, the difference between the two 850 C tests show that the slopes of the curves, at least below zero, are a property of the abrasive and not the thermobalance.

In all cases except at the lowest temperatures of 500°C and 550°C, the curves pass through a minimum. Up to 750°C the minima tend to rise to higher weight recordings with temperature but above this temperature the minima decreased to 800°C then rose to 850°C; thus the curve plotted through these points, shown in figure 5.5, passes through a minimum

- 103 -

Cont'd.

and a maximum. The rise above 800 C is probably due to the earlier onset of oxidation to silica with temperature rise, and the preceding maximum is probably related to the minimum of figure 3.5.2.

In figure 5.6 the time required to reach each minima (figure 3.5.3) is plotted against temperature using a log time scale and a straight line is obtained. A regression analysis showed the equation to be

 $\log t = 6.54 - 0.0083T$ 1 T=temperature in oc where E= time in hours with a coefficient of correlation of 0.998 which for 4 degrees of freedom is more significant than 99.9%. From this regression two points may be noted. In view of the small weight changes involved this significance demonstrates the high accuracy of the equipment. Secondly, if it is assumed that the minima coincide with the onset of oxidation to silics, then from equation 1, the formation of a siliceous layer at 1000 C would be expected after ca 1 minute. It seems likely that the formation of this layer will assist wetting of the abrasive by the bond and this may be significant in the thermogravimetric and strength tests on pellets - it was after about the same time interval that the effects of possible agglomeration became evident.

Cont'd,

104 -

- 105 -

5.6 The Effect of Bond Fusibility.

To show this effect it was decided to use fine white alumina pellets which it was thought would show the effects more clearly and avoid the chemical effect of silicon carbide, ie the possibility of carbon precipitation by partial oxidation. The problem is associated with the residue of carbon that remains after decomposition and may still remain, after firing, (at the centre of large wheels in particular). In these tests three bonds were used, designated ARF, RF and RE of which ARF was the least fusible and RE the most (see section 2, figure 2.1). The results of the experiments are shown in figure 3.7.

In section 5.1 to section 5.4 the basic mechanisms of binder removal were examined, where it was shown that oxidation starts at about 400°C. However, this does not indicate how oxidation can best be done in practice. It seems reasonable that there exists an upper temperature limit above which burn-out rate decreases due to entrapment by fused bond. If such a limit exists heating after 40°C must be controlled.

It can be seen from figure 3.7 that no entrapment occurred up to and including 1200°C in pellets that contained ARF bond, the pellets that contained the less refractory RF bohd, however, exhibited entrapment at 1200°C but not below, while the very fusible RE bonded pellets Cont'd, entrapped carbon as low as 800°C, resulting in protracted burn-out which then appeared to stop completely at 1200 C. it is concluded that for the ARF bond there is no optimum burn-out temperature range as first envisaged. However, the tests show that binder in product containing RF bond must be removed below 1200 C, ie the optimum oxidation range is 400 C to 1100 C. The optimum range for RE appears to be 400 C to 700 C, although the effect of entrapment does not appear to be excessive at, and below, 1000 C. It is therefore proposed that to obtain the maximum rate of binder oxidation the following programme should be used: rapid heating up to 400 C; controlled heating to 700 C; rapid heating to top temperature. However, cettain considerations should not be overlooked, for example, the possibility of inverse binder migration, or possible damage to the wheel by excessive thermally induced stress. Furthermore in tunnel kilns control over the rate of heating may not be adequate to ensure complete binder removal by 700 C and therefore controlled heating rate to 1000 C may be necessary. Above 1000 C continued burn-out appears unlikely, from the tests, and consequently subsequent heating rate may be faster.

106 -

A very important factor in commercial firing operations is the temperature difference that usually exists across a wheel, often from top to bottom, when the bottom is invariably

Cont'd.

lower than the top, If, as was suggested in section 5.5, bond fusion reduces porosity of the surface and thus impedes ingress of air (or CO) into the mass, this difference may become important because a layer on the top and sides of a wheel could cause a premature entrapment of carbon still present towards the bottom centre where the temperature is lower. Probably for ARF bonded structures this effect is not important and for RE also it is probably slight, since at 1200 C where entrapment by this bond occurs the product will be approaching maximum temperature and the temperature difference will itself be small. For RE bonded products however, the situation is rather different. Over the optimum burn-out range of 300 C (from 400 C to 700 C) the top to bottom temperature difference is often 100 C or more. If it is assumed that this difference is the only temperature gradient (ie: if the contribution necessary for heat transfer is ignored) then 33% of the burn-out range is wasted. From 400 C to 700 C the heating rate is usually linear and therefore if the gradient were eliminated the time available for oxidation would be increased at least 50%.

The reason for the severe entrapment of carbon by RE bond must be associated with its greater fusibility. The q uestion arises whether entrapment is due to its overall fusibility or whether both its fusibility and its entrapment characteristics are due to the amount and fusibility of some specific constituent.

- 107 -

It can be seen from figure 2.1 that ARF which gave no entrapment problem contains no flux while RE and RF do : furthermore, RE contains approximately twice the amount. A theory is that entrapment occurs when the fused, vitrified or mobile components of the bond are sufficient to fill the intestices of the remaining solid bond components - if the fluid in the bond is less than this the bond remains porous but if it is greater, a continuous and impervious structure is possible compacted by surface tension. The flux used in RE and RF is very fusible and will therefore form a fluid at a relatively low temperature. In RF this flux constitutes ca 27% of the bond so that when it is fused it will equal 37% of the residual solids. In RE the flux constitutes 57% which is 135% of the remaining solid. The packing factor for these bonds is about 60%.

Therefore, in RF, there is insufficient flux to satisfy the proposed criterion for entrapment at its melting point and therefore entrapment cannot occur in RF until the temperature is reached where the remaining constituents enter into the vitrification process (probably by dissolving into the fluid and thus increase its volume). In RE there is more than enough flux and entrapment can occur when this reaches mobility. In the light of this theory it should be possible to improve the characteristics of this bond (RE) by using a more fusible flux but in much smaller proportions, Cont'd.

. 108 -

eg 60% (or less) of the balance, which corresponds to a reduction of 20% (or more).

5.7 The Kinetics of Burn-out.

From an examination of silicon carbide pellets fired at 1250 C through to 1350 C, shown in figures 3.6.1 to 3.6.3, two types of pellet can be distinguished, those that are wholly or partly friable and those that are hard throughout. During correct firing the following three processes must take place: binder burn-out, bond vitrification (fusion) and wetting of the abrasive by the vitrified bond. It is proposed that the distinguishing factor is wetting. In the hard structures a continuum of silicon carbide and bond was formed but in the friable structures it was not. The formation of a continuous structure affects more than mechanical properties however. Any mixing, as first prepared, consists of grains of abrasive surrounded by a fine powdery bond material and held together by binder. When burn-out commences this mixture is rendered brown/black by caramellisation of the binder, shown in figures 3.6.1 to 3.6.3 by pellets fired for 20 seconds. On further firing these pallets, up to three additional zones appeared (described in section 3.3) thus making a total of four. The first of these zones was lighter in colour while the second was darker. It was surprising therefore to find

Cont'd.

- 109 -

an intermediate light zone between two dark zones: it seems extremely unlikely that the residue of carbon should pass through a minimum. It is suggested that the phenomenon is the result of changes in optical properties which are related to the observed duality in mechanical properties.

For a continuous structure to develop, by wetting, the bond must be in a fused (or semi-fused) state which will transmit light readily. The bond in its initial powdery form appears white owing to scattered reflection of light near the surface of the mass. It follows that the second zone develops because the binder has been reduced in amount by decomposition or oxidation to a level where the light scattering effect of the bond predominates over absorption by carbon, but when the continuous state is reached the bond ceases to scatter, and light is absorbed by the residual carbon. The outer most zone is obviously the carbon free structure aimed for during manufacture. It can now be seen that the four structures observed in section 3.3 were :

A.Discontinuous with a high carbon contentB."low"C.Continuous""D."and carbon free"

These four structures are similar to those observed in the "soft core" defect shown in figure 1.2 and hence the same arguments can be applied. Cont'd.

110 -

It is apparent from figures 3.6.1 to 3.6.3 that the effect of temperature and structure on the first zone A, developed after firing for 20 seconds, is negligible. This is probably a consequence of the method of representation had weights been quoted, differences may have been seen.

After 40 seconds firing differences became clear. In order to compare the relative effects of temperature and pressure it is convenient to compare the most porous pellet (fired for 40 seconds) in figure 3.6.1 to the least porous, fired for the same time, in figure 3.6.2. It is then seen that there is very little difference even though the temperatures differed by only 50°C while the compacting pressures were in the ratio 5:1. Again, if figures 3.6.2 and 3.6.3 are compared, in like manner, the same is found. From this it is concluded that temperature has the greater effect. After firing for 1 minute compacting pressure has distinctly more influence (on the progress of each zone), while temperature has little effect if any.

These observations compare favourably with the thermogravimetric tests on pellets. In section 5.4 the abrupt change in rate of weight loss with time when pellets are fired at 1000 C was considered. It was concluded that the transition at stage IV of pyrolysis from decomposition to Cont'd.

- 111 -

oxidation could be a contributing factor and the argument was based on expected sensitivities of decomposition and oxidation to permeability. It is interesting that even though the temperature in that test was lower than in the present series the discontinuity occurred after about the same time interval, and it seems likely that the change in sensitivity to porosity in each test is related at least in part to the same stage IV characteristic.

So far compacting pressure, structure, porosity and permeability have been assumed equivalent, and it is significant that for firing times up to 1 minute, compacting pressure is the predominant factor. However, when bridging occurs between grains of abrasive by bond fusion, pores will tend to become discrete and permeability will not be controlled solely by the volume of porosity: it will also be controlled by the effectiveness of bridging. For tests of 3 minutes and over the continuous structure becomes a major factor and most of the observations can be explained by the effect of temperature in this way. A further point to be noted is that glass does not wet carbon and therefore bridging is likely to be most effective in zone D.

This concept is consistent with both the thermogravimetric and the compressive strength experiments where the elimination of binder at and near the pellet surface

Cont'd.

was also proposed to account in part for the observations. In this context the effectiveness of bridging in zone D is particularly significant. It was also suggested in section 5.5. that at 1000°C the formation of a siliceous layer on the abrasive probably takes cal minute to form and that the formation of this layer should assist wetting.

After firing for 3 minutes at 1250 C (figure 3.6.1) the following observations can be made: the pellet compacted to 1.1 t.s.i. completely burnt-out to structure D; the pellet compacted to 2.2 t.s.i retained a triangular zone C; the next in the series contained B with a slight amount of A, and the fourth pellet, all four zones, including a much larger quantity of A. The first conclusion to be drawn is that porosity has a profound influence on the progress of each stage. However, the rate of contraction of these zones are not equal. Comparing the 4.5 with the 5.6 t.s.i pellets it is seen that zone A has virtually disappeared at the lower pressure and zone C is near the centre but the total defective areas are approximately equal - the difference lies mainly in the width of each zone. Furthermore, in the 2.2 t.s.i. pellet, zone C is much more extensive than in the two previous pellets.

An initial assessment of the results at 3 minutes suggests a relationship with temperature distribution within the pellets. As each zone approaches the centre of the Cont'd. pellet it tends to become wider and if one correlates these zones with temperature, this pattern would be expected. However, the pellet which burnt-out most was compacted least and should therefore have the lowest thermal conductivity while the pellet compacted most burn-out least. This is clearly incongruent. Furthermore, temperature has been shown to have little direct effect on burn-out rate and therefore the distributions of the zones must be associated with diffusion.

It has been proposed that zone A has a discontinuous structure and consequently burn-out will depend upon diffusion of air from the surface to the centre of the pellet; thus entrapment within this zone by lack of permeability in the surrounding continuous structure may be described as macroscopic. However, zone C is continuous and it seems likely that carbon may be trapped microscopically by fusion of the bond around residual carbon precticals and burn-out of this carbon is controlled by diffusion through the bond.

The pellets pressed to 4.5 and 5.6 t.s.i support this explanation of two types of entrapment since one would expect the removal of carbon entrapped macroscopically to be much more sensitive to gross porosity than carbon entrapped microscopically. Also zone A was eliminated in less than 10 minutes but zone C persisted for longer than 14 hours which further suggests two different mechanisms.

Cont'd.

The aim of compacting is to press the abrasive grains closer together and it is unlikely the bond will be compacted much but exuded into surrounding voids. It is therefore not surprising that retentions of zone C in the two pellets pressed to 4.5 and 5.6 t.s.i were almost idential. At the two lower pressures the same is not true and it is proposed that this difference arises from the different dependencies of macroscopic oxidation and bond fusion on time and temperature.

The bond used to prepare the mixings consisted of a number of constituents varying widely in fusibility. Consequently the bond vitrifies over a very large temperature range: as heating progresses the least refractory constituent will fuse or soften first, then as the temperature continues to rise other constituents probably dissolve into the adjacent fluid. Time must be required for this process although temperature is probably the predominant factor. In the case of carbon oxidation it is proposed that the reverse is true: temperature must have some direct effect on reaction rate although the main factor is time elapsed. since burn-out requires diffusion. An additional point may be noted here: from the heat transfer tests it was concluded that for silicon carbide the pellet would require

- 115 -

is approximately the time interval of the present discussion. Considering these factors together the following theory emerges: because of the very open structure, binder in the 1.1 t.s.i pellets burnt-out very rapidly before the bond had fused sufficiently to cause entrapment; at the two upper pressures the lack of permeability delayed burn-out sufficiently for the bond to reach a higher temperature, fuse to a greater extent and thus entrap carbon microscopically; the pellet compacted to 2.2 t.s.i was presumably borderline, is time was not quite adequate to remove all of the binder before fusion but microscopic entrapment was not sufficiently severe to lead to a very protracted burn-out.

In section 5.6 a criterion was evolved which stated that entragment occurred when the fluid content of the bond is sufficient to fill the interstices of the remaining solids in the bond and this conclusion was drawn from the effect of bond composition on the rate of burn-out at various temperatures. No mechanism was proposed other than the bond becoming impervious once the criterion has been met. If one considers only macroscopic entrapment the criterion can only operate by forming a completely impermeable structure in conjunction with the abrasive. If this is obtained it is difficult to see how any burn-out could have occurred in these tests performed at 1250°C and therefore it is proposed that the criterion determines microscopic entrapment.

Cont'd.

Applying this concept the previous conclusions can be refined as follows: in pellets compacted to 1.1 t.s.i which were the most porous, burn-out was completed before the entrapment criterion was satisfied while in the less porous pellets it was not - in the 4.5 and 5.6 t.s.i pellets the accumulation of fluid, while carbon was still present, was sufficient to fill the interstices of the remaining solid bond constituents resulting in a burn-out period of longer than 1½ hours.

In section 3.3 a brief description of the pellets was given where it was noted that the pellets compacted to A.1 t.s.i and fired for 3 minutes at 1300°C had burnt-out completely. This observation is not consistent with the general trend at this pressure and temperature and the anomaly must be assumed to be due to experimental error. Also, the pellet compacted to 2.2 t.s.i and fired for 10 minutes appears in figure 3.6.2 not to be very carbonaceous. However, the pellet was black at the core although contrast is poor throughout this photograph. In general the results obtained at 1300°C compare favourably with other temperatures.

At 1300 C in particular, and for the l.l t.s.i pellets fired at 1350 C, a phenomenon that was not so obvious at 1250 C was apparent: the removal of carbon in a continuous structure (is from zone C) differs fundamentally from the removal of carbon from a discontinuous structure (ie: from

117 -

Cont d.

zone A). In all the cases of burn-out from zone C no reduction in its size occurred but it was observed that the zone persisted for a period of time and then abruptly disappeared to leave the carbon free zone D. This agrees Well with the idea that the carbon of zone C is entrapped microscopically, that massive permeability is not the primary controlling factor, and consequently burn-out, at this stage, is fairly even throughout the pellet.

At 1300 C it is particularly noticeable that porosity affects the total time required for complete removal of carbon. For the same firing the porosity of the pellet will affect parmeability and it is possible that this will have a direct rate controlling influence on burn-out, but in the light of the above theory it is difficult to see how it can make any major contribution simply by limiting air diffusion into the pellet - it has been argued that the rate controlling mechanism is diffusion of oxygen in the fused or partially fused bond. However, the overlap theory is itself sufficient to explain the effect. It has been observed that porosity is the principal factor controlling the rate of burn-out in the early stages and consequently for any given temperature of firing the porosity will determine the amount of carbon remaining in the pellet when microscopic entrapment occurs. Obviously the more carbon there is entrapped by the bond the longer it will take to Cont'd.

- 118 -

burn-out under similar conditions. An obserwation that supports this is that decreasing the porosity reduces the width of zone D that surrounds the core. It has been shown that zone A is removed by oxidation from the surface inwards and if reducing the porosity inhibits this process then the area over which entrapment occurs must be larger for lower porosity samples.

From a general comparison of the tests (1250 C to 1350 C) it is obvious that raising the temperature leads to more protracted burn-out rates which supports the idea that raising the temperature reduces permeability by promoting bridging, but an affect may contribute which can be considered the converse of the above mechanism. It has been shown that microscopic entrapment can be thought of as overlap between two mechanisms, viz: zone A burn-out and bond fusion and decreasing the porosity delays the former so that more overlap and hence more entrapment occurs. It has been shown that porosity is the main factor controlling this oxidation and so raising the temperature will again cause greater overlap but by accelerating fusion. In the tests both temperature effects probably delay burn-out (ie the attainment of zone D).

Close examination of the pellet compacted to 1.1 t.s.i and fired for 2 minutes at 1350°C, and to some extent the pellet compacted to 2.2 t.s.i, suggests that firing

- 119 -

temperature modifies the zone sequence A to B to C: instead of zone B moving through the pellet across section from surface to entre it merely darkens so that zone A merges into C, and at the higher temperature the bond fuses to form a continuous structure despite the large amount of residual carbon. This theory is developed from the idea of bridging in zone D (the outer zone), producing a very impermeable layer. The light coloured zone B is presumably related to a time effect and it is bordered by two fronts, viz: the point at which burn-out is well advanced and the point at which fusion is sufficient to satisfy the microscopic entrapment criterion. If an impermeable layer develops the progress of the first fronts will be fixed (or very much slowed down) and zone B will not move closer to the centre but the result will be a general darkening: as the temperature distribution levels out and the bond becomes evenly fused throughout the pellet, light striking the surface of the pellet will penetrate further into the structure to be absorbed more completely by carbonaceous matter. Consequently, in the case of pellets fused at 1250 C various stages of burn-out, achieved after 3 minutes, could be related to porosity and hence permeability but extrapolation cannot be made to include pellets fired at 1350 C for the same time. After shorter firing times zone B exists, but then porosity and time become the controlling

- 120 -

Contid.

factors and the effect of temperature and its concomitant effect on permeability are minimal.

5.8 The Thermodynamics of Burn-out.

In the tests performed on alumina pellets (section 5.6) the defects were matt tending to be brown to black at low temperatures and grey to black at high temperatures. In the silicon carbide pellet tests it was reported in section 3.3 that early forms of zone C also tended to be matt but it became more reflective with time. The shiny black structure is similar to the shiny black defect shown in figure 1.1 where it was suggested that while the very friable core was probably associated with binder carbon, the hard shiny core was associated with carbon from the silicon carbide. This is still tenable although the SiC pellet tests imply that the mechanism is more complex than the original concept might at first suggest.

It has been argued that initially decomposition and oxidation remove carbon distributed in a porous discontinuous structure, and that the friable defect is representative of this stage. However, at a critical point in the fusion of the bond microscopic entrapment of carbon occurs. Beyond this point oxidation of the carbon entrapped by the bond continues, until its removal is complete. However, the latter stage is probably an over simplification.

Cont'd.

It has been shown in section 4 that if oxidation is restricted, silicon carbide will tend to precipitate elemental carbon. The restriction applied in that section was that the system should be closed. This restriction is not kinetic but thermodynamic and is in fact a special case of a more general restriction. It can be shown not to be kinetic by considering the mechanism of oxidation of free flowing grains of pure silicon carbide. It was stated in section 1 that, as with metals, pure silicon carbide tends to form a protective layer of oxide on its surface, but this very severely limits the availability of oxygen, kinetically, and can in fact bo used to explain the parabolic rate law of oxidation. However, free flowing silicon carbide does not blacken when oxidised in air or oxygen. Examination of the various systems considered in section 4 shows that when silicon carbide is oxidised to silica and carbon the partial pressure of residual oxygen is extremely low, and in fact the restriction simply allows equilibrium to be reached and closing the system is seen to be an indirect way of lowering oxygen potential. In section 1 it was reported that if silicon carbide is heated in carbon monoxide to 1300 C it is blackened and the reaction proposed was :

sic + 200->30 + 510

In this system CO is being used as a source of oxygen to Cont'd.

- 122 -

partially omidise SiC; but the use of CO in this way is only another method of restricting oxygen potential. Furthermore, the activity (or fugacity) of the oxygen will be given by the equilibrium :

In the pellet tests during the oxidation of zone C one can imagine a permeable structure of silicon carbide grains surrounded and joined by a siliceous bond containing entrapped carbon. This carbon will oxidise in the same way as silicon carbide, is oxygen will diffuse through the glass. However, reaction with carbon will reduce oxygen activity, and if equilibrium is assumed, this will be determined by equation 3. Consequently oxidation of the underlying SiC will be thermodynamically indistinguishable from equation 2, and if kinetics are favourable the SiC will blacken. It is proposed that under the conditions of tests this mechanism is kinetically favourable, that it is responsible for the shiny state of zone C, and that the same must be true when the defect is incurred during commercial firing.

In section 1 it was reported that while CO blackened SiC at 1300°C it was unaffected at 1200°C. It was suggested in the same section that this was kinetic, and the stability Cont'd. of carbon in a closed system, found in section 4 supports this. In the pellet tests the shiny black core was pretienes work observed at 1250 C. Unfortunately no reference was found for this temperature: but if the temperature at which CO blackens pure SiC is just above 1250 C it is still likely that blackening should occur in the pallets for the following reason. The tests reported in section (were performed on pure silicon carbide and consequently all the solid phases present (notably silica) would have unit activities. In the pellet experiments bond was included and as reported in section 2 it contains a high proportion of metal oxides including ca 15% alumina. Consequently in the pellets there exists a low activity sink for silica which will promote any reaction involving silica as a product including equation 2.

From the above theory a criterion of discolouration can be developed. It was shown in section 4 that for system SiC/SiO /gas the predominant reaction to be expected at 2 high temperature is :

 $\operatorname{S1C} + \frac{3}{2} \xrightarrow{0}{2} \operatorname{S10} + \operatorname{C0} \qquad \dots \qquad (\frac{1}{2})$

but when carbon is precipitated the equation

$$\frac{10}{2} + 0 \xrightarrow{3} 10 + 0 \qquad \dots \qquad (5)$$

should proceed. The problem is to find the point beyond Contid.

- 124 ,-

which equation 5 becomes more likely than equation 4, ie: when

Equation 4 can be resolved into equation 5 and

$$C + \frac{1}{2}0 \longrightarrow CO$$
 (7)

Therefore the criterion for discoleration is that the free energy of exidation of carbon to carbon monoxide is greater than zero, is: when

$$\Delta G_{7} = 2\Delta G_{7}^{0} + \frac{RT}{2} \ln \frac{p^{2}c_{0}}{p} > 0 \qquad \dots \dots \dots \dots \dots (8)$$

whence
$$53400/T + 41.8$$

 $\frac{p_{C0}^2}{p_{0_2}} > e^{\frac{53400}{T} + 20.6}$ (10)

At high temperature carbon monoxide is the most stable oxide of carbon and if for simplicity we assume nitrogen (from air) to be absent the atmosphere will consist of oxygen and carbon monoxide. It has already been shown that the partial pressure of oxygen will be low when equation 5 is favoured. Therefore at unit atmosphere pressure the criterion reduces solely to the partial pressure of oxygen Cont'd. and equation 10 reduces to :-

р₀ < е

In previous subsections kinetics were assumed the main factors controlling burn-out. In many of the tests burn-out was not in fact completed. At 1300°C the pellets pressed to 4.5 t.s.i, and less, burnt-out completely but the 5.6 t.s.i pellet did not. In this case considering the general pattern, it is probably reasonable to assume that had the firing been continued, burn-out of these pellets would also have occurred. At 1350°C only the most porous pellets burnt-out and it is possible that the carbonaceous core was stable at this higher temperature.

126

In this discussion on blackening, the removal of carbon from one location is proposed to cause carbon formation at another, but no correspondence between the amounts of carbon has been suggested. In the tests where burn-out occurred the rate of removal of carbon must have bee n greater than the rate of precipitation. However, in section 5.8 reference was made to the likelihood of bridging in the outer, carbon free, zone: furthermore, with oxidation in this zone both the amount and fusibility of the bond will increase and it seems likely that at high temperature the permeability of this layer could be very low. The oxidation of entrapped carbon lowers oxygen potential by Cont'd. forming CO but if the rate of ingress of oxygen is limited it will be diluted by this CO and its activity will be lowered by dilution. Consequently the amount of entrapped carbon that has to be oxidised to satisfy the criterion proposed above for blackening will be lowered and the ratio of carbon precipitated to carbon oxidised will be raised. The overall reactions may be resolved into three stages as follows: oxygen initially at 0.2 atmospheres pressures, diffuses through an almost impermeable layer of zone D and its partial pressure is reduced, by dilution with CO; the oxygen then reacts with carbon entrapped by the bond so that the oxygen potential of the system is insufficient to oxidise carbon further; oxidation of the silicon carbide is consequently to silica and carbon. If the rate of oxygen ingress is reduced further the reduction in partial pressure of the oxygen by the first stage will be more and consequently the amount of carbon that will be oxidised at the second stage will be less; eventually a point must be reached where the amount of carbon oxidised just equals the amount precipitated (by partial oxidation of the silicoon carbide) and the two reactions balance. Beyond this point carbon will accumulate and the reaction

originally proposed in section 4 will proceed; thus the system becomes virtually closed.

- 127 -

The partial pressure at, and below, which oxidation proceeds by equation 5 is that the amount removed should not exceed the amount precipitated. If we consider 1 mole of oxygen at a partial pressure of p where p 02 min. 02 min. is the partial pressure at which reaction 5 proceeds, then over which there should be a range from p to p 02 min. 02 max. carbon is still formed although some CO is also formed. If the process is considered as occurring in two stages viz oxidation of carbon to carbon monoxide to reduce the partial pressure to p then p is that amount of oxygen 02 min. 02 max. which oxidises as much carbon is precipitated. For 1 mole of oxygen, 1 mole of carbon is precipitated but & mole of

oxygen is required to oxidise this to carbon monoxide and therefore -53400/T - 41.8-26.900/T - 21.0 (12)

$$p_{02 \text{ max.}} = \frac{3}{2} p_{02 \text{ min.}} = \frac{1}{2}e_{-53400/7 - 41-4} \cdots$$

The same arguments can be applied to any source of oxygen, when the criterion may be stated as follows : discoleration is thermodynamically possible only if the oxygen potential of the oxidising agent is insufficient to oxidise carbon to carbon monoxide. It may be noted that carbon monoxide always satisfies this criterion. In the case of oxidation by carbon dioxide two moles of carbon must Cont'd. be precipitated according to the equation

but this will require two moles of CO to oxidise this 2 carbon to carbon monoxide, and therefore

In section 4 it was shown that in a closed system carbon is stable up to 1300°C but not at 1400°C and above, when the reaction

(ie the reverse of equation 2) will tend to proceed. It was reported in section 3.3 that after very prolonged firing times at 1400°C the core changed from black (shiny) to grey/green. This high temperature of firing may not be of great direct practical significance. Nevertheless the observation does support some of the concepts being considered and it is proposed that this was the result of carbon oxidation by the bond according to equation 15, that carbon is therefore not stable in this system and that the system is closed. It was reported in section 3.3 that the outer layers of these pellets had "boiled". This supports the proposition that in the carbon free zone, bridging, assisted by high temperature and oxidation of the SiC, can Cont'd.

129 -

severely reduce permeability since for the structure to be distended it must have been impervious or very nearly impervious. It seems unlikely that carbon removal occurred by ingress of air (as at 1300°C for example) but that equation 15 proceeded as predicted in section 4).

6. Conclusions.

The thermochemistry of binder removal involves two types of reaction viz: anaerobic and aerobic and each of these can be further subdivided as follows :

Anaerobic	1.	Drying
	2.	Dehydration
	3.	Further decomposition involving
		evolution of carbonaceous gases -
		ie caramellisation.
	4.	Macroscopic or primary oxidation.
Aerobic	5.	Microscopic oxidation (of
		which there are two stages, viz:)
		a) Secondary oxidation of
		binder carbon;
		b) Tertiary oxidation of carbon
		resulting from partial silicon

The friable core was shown to be associated with nonwetting of the abrasive by the bond and with the presence of carbon macroscopically distributed. The hard shiny defect was shown to be associated with wetting of the abrasive by the bond and with microscopically entrapped carbon. It was further shown that tertiary oxidation ceased if the ingress of oxidising atmosphere was severely impeded, when

carbide oxidation.

partial oxidation of the silicon carbide to silica and carbon occurred.

6.1 Drying.

Rate controlling factors during drying include heat transfer, water content, bond content and binder characteristics. The main factor was found to be total mass although porosity will tend to limit conductivity. Bond probably helps heat transfer in as much as it displaces air between grains although clay content inhibits drying probably because of its high affinity for water. For glucose, drying may be impeded by the formation of an impervious skin, but dispersing the binder over a large surface area minimises the effect.

Drying may affect later processes by controlling porosity and amount of binder to be subsequently removed. Glucose was found to show the largest weight loss at this stage.

6.2 Debydration.

The temperature at which dehydration commences was found to vary between tests but no cause was apparent. The temperature at which this stage ended was found to be controlled by the bond and it was suggested that the effect was due largely to the presence of clay and its affinity

Cont'd.

132 .

for hydrogen and hydroxyl groups. Rate of heating was found from the pyrolysis experiments on pure binder, to have very little effect, and from the tests performed on pellets it was concluded that porosity and permeability also had little effect.

Dehydration, like drying, reduces the amount of binder to be removed subsequently. Unlike drying it may have a serious disadvantageous effect on porosity due to dilation associated with it since dilation was shown to reduce the oxidation zone width by severely reducing porosity locally. However, it was also shown that the effect of dilation on the morphology of the final carbon residue tends to have an overriding influence and glucose, which undergoes most dilation, oxidises more rapidly than starch which exhibited no dilation, and oxidised slowest. However, starch showed the largest weight loss at this stage and it was concluded that the mechanism of dehydration was important - glucose and dextrin probably dehydrate more by polymerisation than starch.

6.3 Caramellisation.

The final stage of anaerobic binder removal is constituted by the initial part of stage IV of pyrolysis. The significance of this stage found to be determined by the amount of previous dehydration and it was shown that for starch the contribution was minimal. Porosity has little

Cont'd.

- 133 .
effect on the progress of this decomposition although it must have an effect on the point at which it ceases to have a rate controlling influence, since it was evident from pure binder results, in particular, that direct oxidation becomes the rate controlling factor when the products of decomposition cease to protect the residue.

In general it was shown that decomposition products impede direct oxidation and hence promote overlap between binder removal and bond fusion leading to microscopically entrapped carbon. Wheel size is important here since in a large wheel the centre will heat up more slowly and decomposition products will be evolved over a larger period. For large masses the temperature gradients near the surface tend to be steeper and hence inward migration, which was shown to follow from temperature gradients, may also be promoted in large wheels.

6.4 Macroscopic Oxidation.

Macroscopic or primary oxidation follows decomposition and it is terminated when either burn-out is complete or bond fusion occurs. Consequently it is favoured by mechanisms that :

- 1. Promote completion of decomposition
- 2. Accelerate oxidation
- 3. Delay fusion.

Cont'd.

The first of these has been dealt with in the previous subsections and the third will be considered in section 6.5. In this subsection, those factors which directly affect oxidation rate are considered and probably the most important single factor is mass transfer by diffusion, controlled by permeability.

In the discontinuous structures, porosity has been shown to be the main factor determining permeability and hence oxidation rate, and this structure is primarily associated with macroscopic carbon.

The continuous structures are not directly associated with primary burn-out but the two types of structure often coexist and the outer structure may be an important factor affecting the rate at which oxygen (or CO) reaches the 2 discontinuous zone. In the continuous structure actual porosity is less important, as bridging tends to promote the formation of discrete pores with a concomitant lower permeability. The amount of bond and its fusibility (and hence fluidity at firing temperature) may be very important, especially in large wheels: a large mass necessitates a large temperature difference between surface and centre and therefore at the time of primary oxidation (at the centre) the bond will be more fluid, bridging will be more effective and ingress of furnace atmosphere will be limited.

Cont'd.

- 135 -

6.5 Microscopic Oxidation.

The concept of microscopic oxidation was demonstrated most clearly by the silicon carbide tests performed at 1300°C where it was shown that the rate controlling factors were oxygen diffusion and amount of carbon entrapped. In the same section, however, no distinction was made between secondary and tertiary oxidation. From tests on alumina pellets it was concluded that microscopic entrapment occurs when the fluid content of the bond becomes sufficient to fill the interstices of the remaining solid bond constituents.

The amount of carbon entrapped was found to depend upon the rate of removal of macroscopic carbon, as considered in the previous subsections, and the rate of approach to the "entrapment criterion", was found to depend upon rate of heating and the amount and fusibility of fluxes, in particular.

Oxygen diffusion across the fused bond will depend mainly upon temperature and thickness of the bond which will in turn depend upon the amount of bond used and grit size (ie the surface area over which the bonds spread). A very fluid bond will also promote bridging, particularly in the outer carbon free structure, and this will limit ingress of furnace atmosphere and hence the oxygen potential of the gas phase of the structure. This will in turn reduce the oxygen gradient in the bond and thus reduce oxidation rate.

Cont'd.

- 136 -

It was shown that during the early part of microscopic oxidation partial oxidation of silicon carbide to silica and carbon could occur. In this respect the oxygen potential of the gas phase is particularly important since a reduction of this leads to a reduction in the amount of carbon oxidised to carbon precipitated.

6.6 Tertiary Oxidation and Thermodynamic Considerations.

p = -20.900/T - 20.6 0 = e 2(2)

only the reaction

occurs. It was also shown that at very high temperature silica oxidises carbon, (ie equation 3 was reversed). It was further shown that silica could behave as an oxidising agent even in the absence of carbon at still higher temperature,

Cont'd.

when the reaction was

The burn-out of tertiary carbon is difficult to isolate as a distinct stage and it will in fact be controlled by the same factor which controls secondary oxidation, eg the amount of carbon entrapped. Whereas the amount of secondary carbon will depend upon the interaction between burn-out and fusion the amount of tertiary carbon will depend upon the extent of partial oxidation. Thus tertiary oxidation will be promoted by the following: high oxygen potential and hence the amount of secondary oxidation required to satisfy equation 2 at the bond/ abrasive interface; unfavourable kinetics of carbon precipitation; a small amount of secondary carbon, and hence a minimum period over which secondary burn-out occurs. High silica activity may also impede partial oxidation by opposing equation 3 but was shown not to affect the maximum oxygen potential for discolouration.

6.7 Summary.

The two main defects viz: friable core and the shiny black core can be related to the failure to complete the oxidation stages. Matt black friable parts were associated with non-wetting by bond due to the presence of carbon, while the shiny black defect involves the entrapment of carbon on a microscopic scale.

Cont'd.

- 138 -

Rate controlling factors during drying (the first stage of binder removal) include heat transfer and clay content. Drying may affect later processes by controlling porosity and amount of binder to be subsequently removed.

During caramellisation the effect of dilation may be restrictive, at that stage, but helpful in subsequent oxidation due to a greater dispersion of carbon. It was found that the caramellisation stage overlapped the primary oxidation stage to a greater or lesser extent dependent upon the binder used.

When the bond fuses it entraps carbon microscopically and in addition ingress of air or carbon dioxide may be limited by bridging of the bond between abrasive grains. Removal of the carbon may be very slow and controlled by temperature, amount of carbon entrapped and oxygen gradient across the bond.

By thermodynamic calculation it was shown that silicon carbide may be partially oxidised to silica and carbon by air, carbon dioxide or carbon monoxide at a temperature of o T K when :

$$p_{0} < \frac{-20.900/2 - 20.2}{2} e^{-53400/7 - 41.4}$$

and T = 1573 K (1300 C). At higher temperatures carbon reduces silica and at still higher temperatures silica oxidises silicon carbide to carbon monoxide and silicon monoxide. Cont'd.

139 -

- 140 -

7. Future Work.

There are probably three main lines that future work might follow, viz: to expand the tests performed in this project covering more materials and including more variables; to estimate heat and mass transfer, using a suitable model, in wheels subjected to given firing cycles, and to perform larger scale experiments on wheels rather than pellets. These three approaches are considered in a little more detail below.

7.1 Development of Small Scale Tests.

The thermogravimetric work has demonstrated the basic stages of decomposition but stage IV meeds further analysis. Stage IV was shown to involve both anaerobic and aerobic thermochemistry and further study is required to isolate these. Also the determination of the heats of reactions of each stage could prove to be useful. The effects of other wheel components could be examined further, in particular the effect of clays on dehydration. Subsequently the effect of clays on dilation requires examination and dilation itself could be studied further to determine the effects of heating above stage IV (ie above 260°C in the absence of clay).

Dispersion was though to occur in two ways, eg. induced and inherent dispersions. The former was the result of

Contid.

spreading the binder over a large surface area and further experiments to examine the effects of different grain size are required. The second dispersion effect was the result of dilation and two types of work are required here. The first involves interrupted firing of wheels, and the effects of inward migration and loss permeability due to dilation. The second follows from the opposing advantages and disadvantages of dilation eg it is standard practice to use either starch, dextrin or glucose but by blending starch and glucose, for example, a better balance of properties might be obtained and it is suggested that this is examined.

From the tests on alumina pellets it was concluded that it was not only overall fusibility that affected burnout but the amount and fusibility of the more friable fluxes used in the bond. The criterion that the amount of these constituents should be kept sufficiently low to avoid filling the interstices of the other bond constituent requires further examination, and, in particular, the possibility of improving bonds by using the criterion should be investigated.

The effect of bond on silicon carbide discoleration was considered in the light of both the pellet tests and the thermodynamic considerations and it was suggested that whereas the silica activity of the bond tended to promote Cont'd.

silicon cerbide exidation it did not change the criterion for discoleration which was that the exygen potential of the system should be insufficient to exidise carbon. Therefore work is needed to investigate the kinetic effects of low silica activity in the bond and in general bond composition. The silicon carbide pellet tests could also be expanded to include other bonds, abrasive sizes and lower temperatures.

7.2 Heat and Mass Transfer.

When a wheel is fired heat is transferrëd to the surface by radiation and convection, and from the surface to the centre by conduction. Thus calculation requires data on heat transfer to the surface and conductivity data. Work must be performed to determine these. (Also required in this respect are the heats of reactions of binder decomposition and oxidation).

The treatment of transient heat transfer by analytical methods is extremely difficult but Schenck has shown that if a solid is considered as consisting of discrete nodes of finite size, reasonably accurate calculations can be made, by calculating the transfer of heat between nodes. In some cases the errors are less than those introduced by the approximations necessary to make analytical treatment of the continuous system tractable. The method could probably

be adopted for mass transfer if data is obtained for the effects of various parameters on permeability, including porosity, temperature, bond composition and the effects of residual carbon on wetting and hence bridging. The inclusion of mass transfer could also lead to more accurate heat transfer calculations.

From the above type of calculation, burn-out time could be calculated, and with the addition of thermal and mechanised data, internal stresses could be calculated. These stresses would arise partly from temperature differentials and partly from pressure decomposition products and in this connection the amount of drying necessary prior to a particular firing cycle could also be estimated.

The number of calculations involved would obviously be very large and the task could therefore only be undertaken if a computer was available. Theoretically either a digital or an analytical computer could be used although initially a digital computer would probably be better until the method had been perfected. Once the method had been worked out an analogue computer would do the calculations faster, but the expense of setting up modules to represent each node could be high.

7.3 Large Scale Tests.

The type of work envisaged here is the examination of wheels fired in production. From the alumina pellet tests

Cont'd.

it was concluded that firing should initially be rapid to an optimum burn-out temperature, constant until burn-out was complete and then rapid again. Work is needed to find the minimum time required for complete burn-out at the middle stage. The above work (section 7.2) would be helpful but even without it useful data could be obtained by firing large wheels in this ideal way and examining the product. From these tests firing cycles could be made much more efficient particularly if a simple relationship could be found between time at burn-out temperature wheel size and porosity (it has been shown that for the discontinuous structure porosity is the major factor).

The occurrence of inward migration due to the interaction of stage 2 and steep temperature gradients could probably be examined best in large wheels since in small pellets the effect is bound to be less detectable. This migration necessitates condensation towards the cold centre of the wheel of heavy tar-like distillate fractions. Possible beneficial effects of controlled drying should be investigated, since steam evolved from the centre would tend to sweep these fractions outwards towards the surface and prevent them condensing.

144 -

APPENDIX.

The output from the thermobalance consists of a length of record chart, a sample of which is shown as figure A. This is not the most convenient form mainly because of the length of the chart and therefore in this work those graphs are reduced to figures of smaller size in which weight or a function of the weight is plotted on a continuous scale either against time or temperature. In the binder tests weight percentages of burn-out are used for the silicon carbide oxidation studies. In each case recorded weight is read off on the chart at frequent temperature or time intervals and to illustrate this the procedure is now given in detail for figure 3.2.1, section 3.

Figure A is the thermobalance output for the pyrolysis of a sample containing 2% water, 2% starch and 96% silicon carbide (46 mesh) heated at a programmed rate of approximately 50°C/hour. The problem is to present the relationship between temperature and weight in a more convenient form. In order to facilitate comparison with the pyrolysis of pure binders and on mixtures of different compositions the weight scale is expressed as a function of initial binder in the sample. The weight of the sample used was 12.000 gm so that it must have contained 240 mgm starch and this was called 100%. Again to assist comparison the final weight of the mix after pyrolysis is assumed to be zero and therefore since the mixing contains equal parts

Cont'd.

of starch and water the initial weight per cent of the sample must have been 200 per cent. However, due to loss of water by evaporation during mixing and handling this figure is not in fact realised and therefore the initial weight recorded in figure A, viz 33 mgm, is not suitable as a reference point and instead the minimum weight recording obtained after about 12 hours and at ca 650 C is taken as zero: this reading can be seen to be 24 mgm. Between this point and the start of the recording the weight scale changes and several points by an origin shift of 100 mgm and therefore each section of the recording, starting at the end and working backwards is labelled with the number of milligrams that must be added to the recording to obtain continuity; thus the initial weight at zero time and at 20 C becomes 433 mgms and the weight per cent

 $\frac{433-4}{240} \times 100 = 178\%$

Thus it can be seen that mixing and handling caused a weight loss of 22 per cent. By taking weight recordings and repeating the calculation table A was compiled and from the values given in this table figure 3.3.1, section 3, was drawn.

It is obviously not rational nor desirable to present all the results in this detail and therefore in section 3 only the abreviated forms are given.

- 2

Table A.

Temperature	Weight
2	Per cent
20	178
50	177
75	175
100	166
125	129
150	97.5
175	96.5
200	96.0
225	95.5
250	89.0
275	69.0
300	52.0
325	44.5
350	37.5
375	30.5
400	26.4
425	14.2
450	6.0
475	2.3
500	1.0
550 650	0.6

REFSRENCES

1 Gulbransen E.A. Corrosion 21 (3) 76 (1965)

- 2 Wiebke G: oxidation of silicon carbide. (1960)Berichte DKG, 37,5pp 219-226
- 3 Erwin Jr.G:Oxidation behaviour of silicon carbide. J.Amer Ceram Soc. <u>41</u> (1958) p 347-352
- 4 Lea A.C: The oxidation of silicon carbide refractory materials. J.Soc.Glass Tech. 33 (1949) p 27-30.
- 5 Jorgensen P.J: Oxidation of silicon carbide. J.Amer Ceram.Soc. <u>42</u> (1959) p 63-619
- 6 Balmforth W: Universal Grinding Wheel Co. Ltd. Private communications
- 7 Katz A: Mit Forsk.Inst.Verein. Stahliwerke, Svazek C. 2 (1930).
- 8 Kajnarskii I.S.a Degtijarera E.V:Okislajemost Karborundo - Wych Ogreuporor: Metody ce Snizeria. Ogreupory, 2 (1960) p 77 - 84.
- 9 Chapman A.T:, St.Pierre G.R., Porter W.R., Sherlin T.S: Concerning the stable phase of silicon monoxide, Ohio State University. Tech. No. 60-154 (1960)
- 10 Greenwood C.T. Knox J.H., Milne E: High temperature pyrolysis of starch. Chem. Ind. (London) 1878 (1961)
- 11 Gardiner D.G: The pyrolysis of some hexoses and Di-, Tri-& polysaccarides. J.Chem. Soc. C <u>17</u> 1473 (1966).
- 12 Bloede V.J. A comprehensive survey of starch chemistry Chem. catalogue Co.Inst.NY(1928) p 158
- 13 Pictet A., Sarasim J: Isolation of levoglucosan Helv. Chim.Acta <u>1</u> 87 (1918).

- 14 Biggin P: Universal Grinding Wheel Co. Ltd. Private Communication.
- 15 Paradine C.G;RivettB.H: Stastical methods for technologists - The English Universities Press Ltd. (1966)
- 16 Schenck H; Fortran methods in heat flow Ponald P. (1963)











P. YOUNG

FIGURE A











