THE MICROSTRUCTURE OF CEMENTED CARBIDES
PRODUCED BY LIQUID-PHASE SINTERING

by

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SUMMARY

A detailed study has been made of the microstructure of a number of cemented carbides, prepared by liquid-phase sintering. The alloys investigated were of TiC, ZrC, HfC, VC, NbC, TaC, Mo$_2$C, WC, and certain combinations of these, all with cobalt as the binder phase metal. The dependence of the microstructures on sintering conditions and on physico-chemical properties of the alloy systems, has been studied. For this purpose, solubilities of certain carbides in liquid cobalt, and the interfacial energies between certain carbides and cobalt, have been measured.

It is concluded that the carbide grain growth, which occurs during sintering, occurs by solution-reprecipitation processes rather than coalescence. Possible mechanisms of growth have been analysed theoretically. It appears that, in alloys of VC-Co and Mo$_2$C-Co, the growth is controlled by diffusion through the liquid. For the other carbides, other rate-controlling mechanisms are involved. The growth behaviour of WC-Co alloys is untypical in relation to the other carbides. A second carbide, added to an alloy, usually inhibits the growth, especially if it is present as a separate phase.

The cubic monocarbides develop a cubic grain shape during sintering. The degree of rounding of this shape is explained quantitatively in terms of the anisotropy of the interfacial energy.

In all the alloys there is contact between the carbide grains. It is shown that this develops during sintering, towards a state dependent on the relative values of the interfacial and carbide-boundary energies. With the exception of VC, all the carbides form a continuous skeleton in alloys of 20 vol% cobalt. It is shown that this is not necessarily inconsistent with densification processes.

The hardness and relative toughness of the alloys have been measured. The relative effect of the microstructural properties on the hardness, has been evaluated empirically.
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The present work was undertaken in order to obtain a comprehensive understanding of the factors which determine the nature of the microstructure of alloys prepared by liquid-phase sintering, and is, in particular, concerned with the class of alloys known as cemented carbides.

Cemented carbides are extremely hard materials which find use mainly as cutting-tool materials, but which are also used in applications for which very high wear resistance is required, combined with a fairly high strength. They consist of a hard carbide phase dispersed in a metallic matrix which is often known as the binder phase. They are prepared, almost exclusively, by the powder metallurgical technique of liquid-phase sintering. During the sintering process the metallic phase forms a eutectic liquid with a proportion of the carbide phase and eventually the porosity is almost completely eliminated.

Commercial alloys are usually prepared from the monocarbides of the group IV, V, and VI transition metals, either singly or as complex mixtures and solid solutions. These are combined with between about 5% and 30% of the metallic binder phase, which is usually pure cobalt but sometimes other metals or alloys. The mechanical properties of cemented carbides can be chosen within certain limits by suitable choice of the carbide and the amount of binder phase. Thus the hardness of these alloys can range from about 800 up to about 1800 VPN.

The properties of this type of alloy are not only determined by chemical composition but also, quite considerably, by their microstructure. The microstructure of a given alloy is, in turn, determined by the many variables involved in manufacture, and in particular, the variables of sintering. Much research has in fact been concerned with the effect of production and sintering variables on the microstructure, as well as with the relationship between microstructure and properties. However, this research has tended to be centred on single alloy systems in isolation and/or on systems with the complex compositions of commercial alloys. The result is that there is, at present, no comprehensive or complete understanding of the factors which determine the nature of the
microstructure. Although certain factors are known to be of importance and others are thought to be, information and understanding of these are often only qualitative. In certain cases observations are apparently conflicting and a certain amount of controversy exists.

It is the intention of the present work, by the study of a comprehensive range of alloys, to attempt to determine the relative importance of the sintering variables which affect microstructure and, whenever possible, in quantitative terms. For the sake of experimental simplicity the investigation has involved alloys of relatively simple composition and therefore not necessarily of direct commercial interest. While emphasis has been placed on the physico-chemical aspects of the liquid-phase sintering process, the importance of the relationships between microstructure and mechanical properties has been kept in view.

Although the present study is primarily of significance to the production of cemented carbides, it also has relevance to related topics, as for example: the liquid-phase sintering of other materials (e.g. heavy alloys of the W-Cu-Ni type and certain oxide and silicate based materials); the production of high purity carbides and similar materials; and the production and properties of materials involving carbide:metal combinations, such as dispersion strengthened alloys and filament reinforced composites.
1.1. Brief Description of Cemented Carbides

1.1.1. Commercial Production

A basically similar method is used for the commercial production of most cemented carbide alloys, although there are many variations and modifications of this method, depending on the particular alloy and its intended application. Detailed accounts of production techniques, including the preparation of the carbide powders, have been well documented in the book, 'Hartmetalle' by Kieffer and Benesovsky and only a brief background description is given here.

Cemented carbides are produced from the powders of their constituent carbides and the metallic binder. The relevant proportions of powders are milled together, usually with the addition of a pressing agent such as paraffin wax, and the resulting mixed powder is pressed into compacts. Before sintering, the compacts are often presintered in hydrogen at a relatively low temperature (600 - 1000°C), partly to reduce oxides in the powder and partly to give the compacts strength sufficient to allow some preforming by machining. The compacts are sintered in vacuum or an atmosphere of hydrogen at temperatures between about 1250 and 1600°C depending on the composition of the alloy. The sintering temperature is such that the metallic binder forms a eutectic liquid with a proportion of the carbide. Rapid shrinkage occurs and the compacts should attain close to theoretical density. The duration of sintering is usually between 30 minutes and 2 hours.

Another technique, used less commonly, for preparing these alloys is infiltration. In this process a calculated amount of the binder metal is melted on top of a compact of the carbide. The liquid metal penetrates the compact and the resulting microstructure is very similar to that produced by liquid-phase sintering.

In Table 1 are listed a few examples of a very large number of cemented carbide alloys which are produced commercially. Typical values of hardness and strength are included.
### TABLE 1
Some examples of cemented carbide alloys produced commercially (taken from reference 1)

<table>
<thead>
<tr>
<th>Carbide content wt%</th>
<th>Binder phase metal, wt%</th>
<th>Hardness V.P.N.</th>
<th>Transverse rupture strength kg/mm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC: 70 to 97</td>
<td>Co: 30 to 3</td>
<td>850 - 1700</td>
<td>300 - 100</td>
</tr>
<tr>
<td>WC: ~90; TiC ~1; (TaC+NbC) ~2.</td>
<td>Co: ~6</td>
<td>1600 - 1700</td>
<td>140 - 160</td>
</tr>
<tr>
<td>WC: ~80; TiC ~10.</td>
<td>Co: ~10</td>
<td>1500 - 1600</td>
<td>150 - 170</td>
</tr>
<tr>
<td>WC: ~63; TiC ~20; (TaC+NbC) ~8.</td>
<td>Co: ~9</td>
<td>~1600</td>
<td>~130</td>
</tr>
<tr>
<td>TiC: ~7; Mo₂C ~8.</td>
<td>Ni: ~15</td>
<td>1700 - 1800</td>
<td>~70</td>
</tr>
<tr>
<td>Cr₃C₂: 89</td>
<td>Ni: 11</td>
<td>1450</td>
<td>~70</td>
</tr>
</tbody>
</table>

### TABLE 2
Carbides formed by some transition metals (from refs. 2 & 3)

<table>
<thead>
<tr>
<th>System: Ti-C</th>
<th>Zr-C</th>
<th>Hf-C</th>
<th>V-C</th>
<th>Nb-C</th>
<th>Ta-C</th>
<th>Cr-C</th>
<th>Mo-C</th>
<th>W-C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbides formed: TiC ZrC HfC V-C Nb₂C Ta₂C Cr₃C₂ Mo₂C W₂C V₂C</td>
<td>Cr₇C₃ Mo₂C W₂C Cr₂₃C₆</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Stable only at high temperatures.*
1.1.2. Constitution and Phase Diagrams of Cemented Carbides

The simplest cemented carbide alloys (i.e. those which contain only one carbide) can be represented by a ternary phase diagram. Figure 1 is a schematic ternary section taken below the eutectic temperature and shows some of the features of significance in a discussion of such alloys. In this diagram, M" represents the carbide-forming transition metal of group IV, V or VI of the periodic table. The binary system, M"-C; can contain one or more compounds as indicated in Table 2 and as represented by M"C and Y in the diagram. Many of these carbides exist over a composition range of non-stoichiometry. This is particularly marked in the monocarbides of the group IV and V transition metals.

For cemented carbides, it is the compound with the highest carbon content, i.e. usually the monocarbide, which is normally used, since this generally has the most favourable properties. Most ternary alloys, therefore, have a composition along the section, M'-M"C, with a fairly low binder-metal content; at x for example.

In all systems so far studied, the section M'-M"C has been found to have the characteristics of a binary eutectic system (see Table 3). Close examination of the section in the systems WC-Co and TiC-Ni indicates that, in fact, it exists between the carbide and a solution of M" in M'. Thus the ratio of M" to C in the metallic solution is higher than in the solid carbide.

Nevertheless, it is usually possible to regard cemented carbides as binary eutectic alloys for the sake of simplicity when discussing their sintering behaviour and microstructure. Thus, referring to Figure 2, sintering is carried out at a temperature such as T_s, at which the metallic binder forms a molten solution containing a concentration, C, of the carbide. The remaining carbide exists as solid particles. Upon cooling in equilibrium circumstances, most of the dissolved carbide reprecipitates and the alloy has a two-phase microstructure of carbide particles in a metallic matrix. There is virtually no solubility of cobalt in the carbide.

If the overall composition of the alloy moves off the binary section, other phases can appear in the microstructure, e.g. free-
FIGURE 1  Schematic ternary section of a cemented carbide alloy system.

FIGURE 2  The pseudo-binary system of a cemented carbide
graphite or a mixed carbide of the binder metal and the transition metal (represented by Z in Figure 1). Examples of carbon-deficiency phases are included in Table 3 (see also 1.1.5.2.).

Although the above discussion has been confined to simple ternary systems, more complex systems often have the same characteristics since the carbides frequently form substitutional solid solutions to give single phases of the form $M^mM^n(1-x)C$, which behave in the same way as a pure carbide (2)(6) (see also 1.1.3). Alternatively, two carbides can exist separately in the binder metal and be regarded as two separate binary systems (1).

Examples of ternary and pseudo-binary systems which are or could in principle be the basis of cemented carbide alloys and which have been investigated are listed in Table 3, together with some of their significant characteristics.

1.1.3. The Properties of Pure Carbides

Before more detailed aspects of cemented carbides are discussed, it is appropriate to consider some of the properties of pure carbides, since these properties have a considerable influence on the properties of the resulting cemented carbides and their behaviour during preparation. The carbides that are most interesting are the monocarbides of the metals: Ti, Zr, Hf, V, Nb, Ta, and W, and combinations of these. To a smaller extent the carbides, Mo$_2$C and Cr$_3$C$_2$ are also of interest.

1.1.3.1. Constitution

The work that has been carried out on the binary-phase diagrams of the refractory carbides has been excellently reviewed by Storms (3) and more recently by Toth (14). All the monocarbides mentioned above are characterised by a high melting point and a range of non-stoichiometry, as indicated in Table 4. Full stoichiometry is attained only with difficulty in some of the carbides (3), and it seems that vanadium carbide cannot exist at higher carbon contents than WC$_{0.92}$. Except for Mo$_2$C, WC, and Cr$_3$C$_2$, the carbides have congruent melting points, but not at the stoichiometric composition.
### TABLE 3  Some systems of the cemented carbide type

<table>
<thead>
<tr>
<th>System</th>
<th>Extent of investigation</th>
<th>Pseudo-binary eutectic**</th>
<th>Phases other than M' or M'_2Co</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-C-Co</td>
<td>complete</td>
<td>1330 45</td>
<td>Co(_2)W(_2)C; Co(_2)W(_6)C</td>
<td>4</td>
</tr>
<tr>
<td>Ti-C-Ni</td>
<td>complete</td>
<td>1307 12</td>
<td>TiNi(_2)*; no mixed carbides.</td>
<td>5</td>
</tr>
<tr>
<td>Ti-C-Fe</td>
<td>complete</td>
<td>1350 9</td>
<td>TiFe(_2)*; no mixed carbides.</td>
<td>7</td>
</tr>
<tr>
<td>Ti-C-Co</td>
<td>pseudo-binary</td>
<td>1360 6</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>Nb-C-Co</td>
<td>pseudo-binary</td>
<td>1350 9</td>
<td>-</td>
<td>9</td>
</tr>
<tr>
<td>Ta-C-Co</td>
<td>pseudo-binary</td>
<td>1402 13</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>Zr-C-Co</td>
<td>800°C section</td>
<td>-</td>
<td>Zr(<em>6)Co(</em>{23})*; no mixed carbides.</td>
<td>11</td>
</tr>
<tr>
<td>Nb-C-Fe</td>
<td>1050°C section</td>
<td>-</td>
<td>NbFe(_2)*; no mixed carbides.</td>
<td>11</td>
</tr>
<tr>
<td>Nb-C-Co</td>
<td>1000°C section</td>
<td>-</td>
<td>NbCo(_3)*; Nb(_3)Co(_2)C.</td>
<td>12</td>
</tr>
<tr>
<td>Mo-C-Co</td>
<td>1000°C section</td>
<td>-</td>
<td>Co(<em>{x})Mo(</em>{(6-x)})C*;</td>
<td>13</td>
</tr>
</tbody>
</table>

*This phase occurs if the carbon content moves slightly off the pseudo-binary.

**Values of T\(_e\) for other systems are included in Table 8.
Table 4: Properties of pure carbides (references are given in parentheses)

<table>
<thead>
<tr>
<th>Carbide</th>
<th>Crystal structure (3)</th>
<th>Homogeneity range below 1000°C, C:M ratio (3)</th>
<th>Maximum melting point, °C</th>
<th>Heat of formation (-\Delta H), kcal/mol at 293°C (3)</th>
<th>Density gm/cc (6)</th>
<th>Vickers microhardness kg/mm², (50 g load)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC</td>
<td>Cubic (NaCl type; fcc; B1)</td>
<td>0.5 - 0.95</td>
<td>3067 (3)</td>
<td>114.1</td>
<td>4.93</td>
<td>2800(16); 2900(18); 2900(3)</td>
</tr>
<tr>
<td>ZrC</td>
<td>&quot;</td>
<td>0.6 - 0.99</td>
<td>3420 (3)</td>
<td>47.0</td>
<td>6.7</td>
<td>2560(16); 2700(18); 2700(3)</td>
</tr>
<tr>
<td>HfC</td>
<td>&quot;</td>
<td>0.6 - 1.0</td>
<td>3950 (3)</td>
<td>50.1</td>
<td>12.5</td>
<td>2460(16); 2500(18); 2300(3)</td>
</tr>
<tr>
<td>WC</td>
<td>&quot;</td>
<td>0.76 - 0.9</td>
<td>2648 (14)</td>
<td>24.5</td>
<td>5.8</td>
<td>3000(17); 2500(18); 3000(3)</td>
</tr>
<tr>
<td>NbC</td>
<td>&quot;</td>
<td>0.7 - 1.0</td>
<td>3600 (3)</td>
<td>33.6</td>
<td>7.8</td>
<td>1700(17); 1500(18); 2400(3)</td>
</tr>
<tr>
<td>TaC</td>
<td>&quot;</td>
<td>0.8 - 1.0</td>
<td>3983 (14)</td>
<td>34.1</td>
<td>14.5</td>
<td>1460(17); 1500(18); 1600(3)</td>
</tr>
<tr>
<td>Cr₂C₂</td>
<td>orthorhombic</td>
<td>v. small</td>
<td>1875 (3)</td>
<td>5.5</td>
<td>6.7</td>
<td>1300 (3)</td>
</tr>
<tr>
<td>Mo₂C</td>
<td>orthorhombic</td>
<td>0.44 - 0.5</td>
<td>2500 (3)</td>
<td>5.5</td>
<td>9.2</td>
<td>1600 (3)</td>
</tr>
<tr>
<td>WC</td>
<td>h.c.p.</td>
<td>v. small</td>
<td>2780 (3)</td>
<td>9.7</td>
<td>15.75</td>
<td>2200 (3)</td>
</tr>
</tbody>
</table>
Most of the monocarbides are completely soluble in each other in the solid state\(^2\). Notable exceptions are the combinations, ZrC-VC, HfC-VC, and the combinations of the group IV and V monocarbides with WC. In the WC mixed systems, the other carbide dissolves quite a high proportion of WC, whereas the solubility of the other carbide in WC is extremely low\(^2\)(\#15). The systems: TiC-ZrC, TiC-HfC, VC-NbC, and VC-TaC, are of interest because they are only completely inter-soluble at high temperatures\(^15\).

1.1.3.2. Electronic Structure

The electronic structure of the cubic monocarbides has been investigated most recently by Ramqvist\(^{16}\)(\#17)(\#19), who has also reviewed and discussed the subject with respect to the properties of the carbides\(^{19}\)(\#20). Electron spectroscopy (ESCA), and X-ray emission and absorption measurements lead to the conclusion that, in these carbides, there is a shift of electrons such that the metal atoms become positively charged and the carbon atoms become negatively charged. The resulting atomic charge is found to be related to the thermodynamic stability of the carbide.

1.1.3.3. Properties

Some of the properties of carbides relevant to the present investigation are summarised in Table 1. In general, their stability increases from right to left of the periodic system, and from low to high atomic weight of the metal atom. This periodicity tends often to be reflected in the properties of the carbides\(^{20}\). All the monocarbides have a cubic NaCl-type crystal structure except WC which has an h.c.p.-type structure. Mechanical strength values are not included in Table 1 because, since the carbides are very brittle, their strength is very sensitive to experimental conditions and existing data is unsuitable for the purposes of comparison\(^{21}\).

A property to be considered when preparing cemented carbides is the oxidation behaviour of the carbides. In the cubic monocarbides, oxygen can replace carbon atoms in the carbide lattice and this can have a considerable effect on the properties. The group IV carbides are particularly sensitive to this type of oxidation and it is extremely difficult to remove all oxygen from them\(^3\)(see also section 1.3.1.4.).
FIGURE 3 The effect of carbon content on the hardness (Vickers microhardness; load 50g) of certain carbides; after Ramqvist (16)(17)
1.1.3.4. The Effect of Non-stoichiometry on Properties

The properties listed in Table 4 are those for carbides which had, as far as was known, a composition close to the stoichiometric value. It is now known that many of the properties of the carbides are influenced considerably by the carbon content. Ramqvist has shown, for example, that the atomic bond strength decreases with decreasing \( C:M^n \) ratio in TiC, ZrC, HfC, and VC, but increases in NbC and TaC.

Of particular relevance to the present investigation is the variation of hardness with stoichiometry which has been determined by Ramqvist\(^{(16)(17)}\), for the group IV and V monocarbides. The results of his investigations are summarised in Figure 3. For TiC, ZrC, HfC, and VC, the hardness decreases almost linearly with falling carbon content, but increases markedly for NbC and TaC. Ramqvist also demonstrated that, for a given carbon content, small quantities of oxygen and nitrogen cause a marked increase in the hardness of TiC. The investigations of Ramqvist were exhaustive and explain or confirm earlier, less detailed findings\(^{(3)(21)}\), as well as being themselves confirmed by even more recent studies\(^{(22)(23)(24)}\).

1.1.3.5. The Properties of Mixed Carbides

The mechanical properties of mixed carbides have received little attention. It has been shown, however, that a measurable effect on the mechanical properties of cemented carbides is produced by alteration of the composition of the mixed-carbide, solid-solution phase\(^{(1)(18)}\).

A few investigations on the hardness of mixed-carbide solid solutions have indicated that maxima in hardness can sometimes occur at certain compositions in some mixed systems\(^{(18)(25)(26)}\).

1.1.4. The Mechanisms of Liquid-Phase Sintering

It is convenient to discuss the processes of liquid-phase sintering both in terms of the driving force for densification, originating solely in the thermodynamic properties of the system, and in terms of the mechanisms of densification which involve kinetic considerations.

1.1.4.1. The Driving Force for Liquid-Phase Densification

The main driving forces for densification during liquid-phase
sintering are the reduction in the total surface energy of the liquid by elimination of pores in the liquid, and also the elimination of the solid surface energy of the particles by the spreading of liquid over their surface or by the formation of contiguous boundaries. In the ideal case of complete densification, all the solid and liquid surfaces will have been replaced by solid/liquid interfaces and solid/solid contiguous boundaries. It may be stated generally that two conditions in combination favour shrinkage, viz.: i) a high liquid surface energy; ii) good wetting, i.e. a low angle of contact of the liquid on the solid.

This general conclusion has been expressed in quantitative terms by two, independently derived, theoretical predictions of the capillary forces in hypothetical compacts. For example, the derivation by Heady and Cahn resulted in an expression for the capillary force between two spherical particles:

\[ P_x = \frac{2 \sqrt{2} \gamma_{lv} \cos \theta}{r} \]

where \( \theta \) is the angle of contact and \( r \) the particle radius. Both treatments lead to the conclusion that the force increases with decreasing particle size and also that, for non-spherical particles, it is affected by the amount of liquid phase.

Cahn and Heady were also able to show that for jagged particles, the capillary forces can develop torque and shear forces. Such forces would be expected to lead to particle re-arrangement, the torque forces tending to bring flat faces together, and the shear forces tending to slide these faces over each other.

Some values of \( \gamma_{lv} \cos \theta \) for the case of carbide/liquid cobalt systems are given in Table 8.

### 1.1.4.2. Mechanisms of Densification

Densification during liquid-phase sintering has been studied in some detail on a large range of systems, including cemented carbides. By combination of metallographic studies with measurement of shrinkage, it has been possible to reach a qualitative understanding of the processes involved in densification. However, there is still some confusion with regard to the details of the processes, and a fully quantitative understanding has not been possible.
It is generally agreed that the sintering process may be divided into a number of distinct stages:

i) The heating-up stage.

During the initial heating of the compact, it is clear that a certain amount of solid-state sintering can occur. In the heating up times normally met with, the densification by this process is comparatively slight, but the compact is strengthened by the formation of bonds between particles.

ii) The re-arrangement process.

Upon the first appearance of the liquid phase at or near the eutectic temperature (see 1.1.2.), very rapid shrinkage begins. This has been explained by assuming that the rigid structure of the pressed and heated compact collapses because of dissolution of solid and penetration of liquid at points of particle contact. This process requires that, at certain points of contact, the following condition is fulfilled:

\[ 2 \gamma_{sl} < \gamma_{ss} \]  

where \( \gamma_{sl} \) and \( \gamma_{ss} \) are the solid/liquid and solid/solid interfacial energies respectively. Individual particles or agglomerates are then able to re-arrange themselves to give a closer packing, under the driving forces discussed above and with the liquid acting as a 'lubricant'.

Kingery, in the only quantitative theory of liquid-phase densification yet to be presented, assumed that this stage is controlled by the viscosity of the liquid and will also be affected by a changing pore size. These assumptions lead to a shrinkage equation for the re-arrangement process:

\[ \frac{1}{3} \frac{\Delta V}{V} \approx t^{(1+Y)} \]  

where \((1+Y)\) is close to unity.

No consideration seems to have been given to the fact that the binder phase also becomes 're-arranged' on melting, thereby also contributing to the overall shrinkage.

iii) The solution and reprecipitation process.

With sufficient liquid phase, the re-arrangement process described above could alone lead to complete densification. However, in many
systems, including most cemented carbide alloys, the volume of liquid is insufficient to fill the free volume between the solid particles, even if they were to achieve closest packing. In fact, it is to be expected that the particles will gradually form a 'locked' array by forming contiguous boundaries long before close packing is achieved (see iv). Therefore, a process other than re-arrangement must exist to account for the observed densification.

It is likely that the most efficient means of solid transfer is by diffusion through the liquid phase, coupled with a process of dissolution and reprecipitation. By assuming that there is complete wetting of the particles by the liquid and that the pore size in the compact is related to the solid particle size, Kingery derived expressions for shrinkage by such a solution-precipitation process. Kingery's model involves the dissolution of material from particles at points of near contact and reprecipitation elsewhere, as a result of which the particles move towards each other. In effect, this leads to a change to a particle shape that has closer packing. When the process is controlled by the rate of diffusion through the liquid, Kingery's treatment leads to the equation:

\[ \frac{\Delta V}{V_0} = 3 \left[ \frac{6k_2Dc_0}{k_1RT} \right]^{1/3} \cdot \frac{1}{r} \cdot t^{3/2} \]  

where \( k_1 \) and \( k_2 \) are constants of proportionality and \( \delta \) is the thickness of the liquid film between the particles at points of near contact (other symbols are defined in Appendix 1).

Unfortunately, as well as having certain weaknesses, this model is extremely difficult to confirm experimentally, because both this process and the re-arrangement process would be expected to occur simultaneously. Results have been presented which were claimed to verify the model for such systems as WC-Co and mixed oxide systems, but as pointed out by Exner and Fischmeister, the verification involved mathematically erroneous interpretation of the results.

The results of shrinkage measurements do, however, indicate two distinct stages; a very rapid shrinkage rate at the beginning of sintering and lasting up to a few minutes, followed by a period of slower shrinkage which leads to almost complete densification. The relative duration of the two stages depends to some extent on the
sintering temperature and the amount of liquid phase. Kingery's equations, even if incorrect in detail, serve to illustrate many of the parameters which are important in determining the rate of any solution-reprecipitation process, viz: the liquid surface energy, $\gamma_{lv}$; the solubility of the solid in the liquid, $C_0$; the particle size $r$; and the mobility of the solid constituent atoms, $D$. Since, however, the model demands the condition of complete wetting of the solid by the liquid, a variation in the degree of wetting is not allowed for.

iv) Coalescence.

There is now little doubt that, during liquid-phase sintering, contiguous boundaries are developed between particles. The model of Kingery is based on the necessity for complete wetting and it was formerly considered that direct contact between particles must only develop to any great extent in the later stages of sintering. Furthermore, such contact, it was supposed, would cause a halt in the solution-reprecipitation and re-arrangement processes. Shrinkage would then only be able to occur by a solid-state sintering process. This was called the 'coalescence' stage of densification.

The results of contiguity (a measure of the degree of contact, defined in section 1.1.5.) measurements by Gurland on WC-Co and TiC-Co alloys seemed to confirm this interpretation. However, subsequent measurements on the WC-Co system and on other carbide systems have indicated that contiguity is relatively large at the beginning of sintering and tends towards some lower but finite value as sintering proceeds (see also 1.2.3.). This invalidates one of the basic assumptions of the theory.

However, studies of particle growth in cemented carbides have shown that the formation of contiguous boundaries is not inconsistent with the functioning of a solution-reprecipitation process, provided that there is a distribution of particle sizes. Furthermore, metallographic observations indicate that the formation of contiguous boundaries can be associated with the moving together or change in shape of the particles involved. Therefore it is possible that a model, similar in form to that of Kingery, could be proposed without the restrictive condition that
there is complete wetting.

Nor is the presence of contiguity inconsistent with the function of a re-arrangement process, since it is quite conceivable that groups of contiguous particles can move and re-arrange themselves. This could continue until a single, continuous skeleton of particles is formed.

1.1.5. A Brief Description of the Microstructure of Cemented Carbides

1.1.5.1. The Normal Microstructure

Figure 1 shows a microstructure which, though not of a commercially-produced alloy, serves to illustrate the main features of the microstructures of cemented carbides in general. The microstructure consists of grains of the carbide dispersed in the metallic binder phase. In some alloys there is more than one carbide phase, but their microstructure is very similar.

The appearance of a microstructure observed at room temperature, probably reflects quite closely the situation during sintering, since the main change which occurs during cooling is the precipitation of some dissolved carbide, mostly onto existing solid particles. This point is mentioned because it is of some importance if metallographic studies are to be related to processes which occur during sintering.

The appearance and distribution of the phases in a microstructure of the type shown in Figure 1, may be described - and to a large extent quantitatively - in terms of a number of parameters. These are described briefly here and will be treated more fully in later sections.

1) The volume fraction of the binder phase, \( \alpha \).

This is a simple function of the composition of the alloy and requires no formal definition. Under certain cooling conditions the binder phase may contain very fine precipitates of intermetallic phases which result from solid-state precipitation from supersaturated solution. These will, of course, not be present during sintering.

*Footnote: The term 'grain' is frequently used to describe the carbide particles in cemented carbides.
FIGURE 4  A microstructure showing the characteristic features of a cemented carbide.
(TaC - 20 vol% Co,  1800 X )
ii) The carbide grain size.

A convenient means of describing the carbide grain size is with the parameter, $\bar{d}$, the mean intercept length, defined as the average length of intersection through the carbide grains, generated by a random line \(^{(45)}\). This parameter has the advantage that it is relatively easy to measure and requires no assumption with regard to grain shape.

iii) The carbide grain size distribution.

In a cemented carbide, the grains of the carbide are not of uniform size because of the inevitable size variation in the original carbide powder. It is possible to measure the size distribution of spherical particles from a two-dimensional section fairly accurately \(^{(45)}\), but for the grain shapes usually encountered in practice, this measurement is difficult or impossible.

iv) Grain shape.

Carbide grains in a metallic matrix are found to take up characteristic shapes during liquid-phase sintering; e.g. the grains in Figure 4 are cubes with slightly rounded edges and corners. The characteristic shape is usually distorted by impingement of the grains.

v) The contiguity, $G$.

In all cemented carbide alloys the carbide grains impinge on one another and form a certain proportion of mutual grain boundaries. Contiguity is a measure of the extent of this contact and is defined as the average fraction of the surface area shared by one grain with all neighbouring grains of the same phase \(^{(46)}\).

vi) The continuity.

The continuity of one phase in a multiphase microstructure is a measure of the degree of connectedness of that phase. It is difficult to define quantitatively, but a possible definition is the probability of formation of infinitely long chains of the phase \(^{(47)}(48)\). A convenient parameter which reflects the continuity of a particulate phase is the number of contacts per particle between particles of that phase \(^{(47)}(48)\). Continuity is not a function solely of contiguity, although in a given alloy system, the properties are probably closely related.

vii) The mean free path of the binder phase, $\bar{\ell}$.

This may be defined as the uninterrupted, mean intercept length of binder phase areas (not grains) measured in a random direction. It is
a measure of the thickness of the binder phase areas, and of the degree of separation of the dispersed phase grains.

viii) The dihedral angle, $\phi$.

In a two-phase microstructure the dihedral angle is the angle formed between the inter-phase boundaries of two adjacent grains of the same phase, at their line of contact. The significance and nature of this parameter has been treated in detail by C.S. Smith [19].

The above parameters have been defined because the properties of the microstructure which they describe are of significance in this investigation. It should be pointed out, however, that they are not all independent but are to some extent inter-related. Thus, $\bar{d}$, the mean free path of the binder phase can be expressed in terms of $\alpha$, $\bar{d}$, and $G$. Both $G$ and $\phi$ are normally determined by the interfacial energies of the system, and it is therefore to be expected that $G$ can be related to $\phi$ and $\alpha$. This interdependence of the microstructural parameters means that it is often very difficult or impossible to alter one of them independently. It will be shown in section 1.1.6, how this leads to difficulty in the interpretation of the observed effects of microstructure on the properties of these alloys.

1.1.5.2. Irregular Microstructural Features

There are a number of features which can occur in a cemented carbide microstructure, that are inconsistent with the simple, two-phase structure discussed above. The most common of these are: porosity, free graphite, and the $\eta$-phase. In most commercial alloys these irregularities must be avoided or kept as low as possible, since they adversely affect the mechanical properties [1][34].

i) Porosity.

In practice, a cemented carbide always contains a finite amount of porosity, although in normal circumstances, this should not be more than a fraction of a volume percent. Even such small fractions can easily be observed metallographically, and porosity is usually assessed according to pore size and amount, by the use of a semi-quantitative estimation that involves comparison with standard micrographs [50].

ii) Graphite.

Free carbon may precipitate in the microstructure of a cemented
carbide if the carbon content of the starting powders is too high, or if conditions of sintering are over-carburising, so that the overall composition of the alloy moves off the pseudo-binary phase region (1.1.2.). The amount of graphite in a microstructure can be assessed metallographically, in a similar manner to that of porosity.

iii) \( \eta \) -phase.

The \( \eta \) -phase is a mixed carbide with the formula: \( M'^3N'^3C \). The \( \eta \) -phase compound, \( W^3Co^3C \), occurs in cemented carbides which contain WC if the carbon content of the starting powders is too low or if the conditions of sintering are decarburising. This phase can form as large crystals in the microstructure and causes marked embrittlement of the alloy. In commercial alloys even extremely small amounts cannot normally be tolerated.

Far less is known about the carbon-deficiency compounds which can occur in WC-free systems. In certain other cemented carbide systems, \( \eta \) -phase compounds have either been found not to occur, or not to be the first product of decarburisation, as is indicated in Table 3. An investigation of the interaction between Ni and Co with the group IV and V transition metal carbides has indicated that lower mixed carbides do not form in these systems.

1.1.6. The Effect of Microstructure on the Properties of Cemented Carbides

1.1.6.1. Mechanical Properties

A considerable amount of research has been devoted to the effect of the microstructure on the mechanical properties of cemented carbides, and in particular WC-Co and WC-TiC-Co alloys. Two recently published works have reviewed this topic in detail and it is dealt with only briefly here.

Because of the interdependence of the most significant microstructural parameters (section 1.1.5.1.), the determination of the precise influence of these parameters on properties is often very difficult. Nevertheless, experimental results indicate in general that the behaviour of these alloys is as might be predicted intuitively.
**FIGURE 5**
The effects of the mean free path of the binder phase, and the cobalt content, on the hardness of WC-Co alloys.

(Taken from Fischmeister and Exner, ref. 55)

**FIGURE 6**
The effect of cobalt content on certain mechanical properties of WC-Co alloys.

(Taken from Exner and Gurland, ref. 53)

**FIGURE 7**
The effects of cobalt content, and of the mean free path of the binder phase, on the transverse rupture strength of WC-Co alloys.

(Taken from Gurland and Bardzil, ref. 54)
i) The effect of binder phase content.

With increasing binder phase content there is an expected decrease in hardness and increase in impact strength of cemented carbides. This is indicated in Figures 5 and 6. For WC-Co alloys the transverse rupture strength passes through a maximum at between about 20% and 40% cobalt (Figure 6).

ii) The effect of carbide grain size.

The hardness of WC-Co alloys decreases with increasing carbide grain size, as would be expected from the behaviour of materials in general. A similar effect has been observed by Sjernberg for WC-TiC-Co alloys, although this conflicts with results given by Kreimer. Experiments with WC-Co alloys indicate that, for cobalt contents between 12% and 20%, the transverse rupture strength passes through a maximum at a WC grain size of about 3 microns (see also iv).

iii) The effect of contiguity.

Somewhat less is known about the effect of contiguity on mechanical properties, probably because of the difficulty of pre-determining this parameter experimentally. Exner and Fischmeister demonstrated that the hardness of WC-Co alloys falls with decreasing contiguity, but the change in contiguity was produced by alteration of the cobalt content. It would be expected that increasing contiguity independently of binder content would cause an increase in hardness in its own right, but this has yet to be shown.

A linear decrease in transverse rupture strength with increase in contiguity has been demonstrated by Gurland, but again the contiguity was not altered independently.

Using a method involving hardness indentations (see 1.3.6.) to measure the energy of crack initiation, Sjernberg has shown that, for a constant cobalt content in WC-TiC-Co specimens, the energy of initiation decreases markedly with increasing contiguity. This would suggest that the strength of the alloy would also decrease with increasing contiguity.

iv) The effect of the mean free path of the binder phase.

By plotting the transverse rupture strength of WC-Co alloys against the mean free path of the binder phase, Gurland has shown that this parameter is probably of greater significance than the...
carbide grain size \(56\). This is shown in Figure 7. The results indicate a maximum strength at a mean free path of about 0.6 microns, regardless of cobalt content. It is to be noted that the sensitivity of strength to \(\bar{I}\) decreases rapidly as \(\bar{I}\) increases above about 2 microns.

The separate effects of \(\bar{I}\) and \(\alpha\) on the hardness of WC-Co alloys is shown in Figure 5. It is clear that the cobalt content has a much greater influence on hardness within the ranges examined. It is also apparent that the influence of \(\bar{I}\) decreases as it becomes larger.

v) The effect of the carbide grain size distribution.

Exner and Fischmeister have shown that, for WC-10\% Co alloys, the transverse rupture strength can be increased if the size distribution of the carbide grains is made very narrow \(55\).

vi) The effect of the carbide grain shape.

There appears to have been no experimental examination of the effect of grain shape on the properties of cemented carbides. It would be expected, however, that angular grains would cause higher local internal stresses in the microstructure than spherical grains. Particle shape is known to be significant in this way for dispersion hardened metals \(57\). Grain shape would also be expected to have an indirect influence on mechanical properties through its effect on contiguity and mean free path of the binder phase \(32\) (section 1.2.3.). A study of the effect of grain shape would be very difficult, since it cannot be altered without changing the composition (or impurity content) of the alloy and also because of its influence on the other microstructural parameters.

vii) The effect of microstructural defects.

Porosity, free carbon, and \(\eta\)-phase all have an adverse effect on the mechanical properties of cemented carbides \(25\) \(53\). Both porosity and graphite reduce hardness as well as strength. The presence of \(\eta\)-phase can increase hardness but reduces strength sharply.

It is clear from the above discussion that knowledge of the effects of microstructure on mechanical properties is largely experimental. Most quantitative descriptions of the effects are empirical. However, Gurland has shown that it is possible to explain qualitatively the observed influence of microstructure on the strength of WC-Co alloys, in terms of fracture and strengthening mechanisms \(35\) \(53\) \(56\). At low cobalt contents and low \(\bar{I}\) values, fracture is
observed to occur mainly through the carbide phase, and the alloy behaves as a brittle material. As the cobalt mean free path increases within this range - either by increases in grain size or by increases in cobalt content - crack propagation is inhibited and the strength increases. At high cobalt contents and high values of $\bar{l}$, the fracture is discontinuous and the alloy behaves in the manner of a dispersion hardened material, in which an increase in microstructural coarseness or a decrease in the amount of the dispersed phase reduces strength.

A similar model to this has been put forward by Kreimer(25)(58).

1.1.6.2. Other Properties

As would be expected, somewhat less interest has been shown in the properties other than the mechanical properties of cemented carbides. Since these alloys are basically mixtures of two or more phases, many of their physical properties and chemical properties, such as conductivity, elasticity, specific heat and corrosion resistance, are influenced more by the relative amounts of the constituents than by the microstructure. In many cases, these properties can be predicted fairly closely by simple laws of mixtures(1)(35).

A notable exception to this is shown by the magnetic properties. These have been studied quite closely because they can provide a simple means of non-destructive testing of cemented carbides.

Since cobalt is ferro-magnetic and the carbides are not, the intensity of magnetisation of a cemented carbide is dependent only on the cobalt content of the alloy. The coercive force, $H_c$, of these alloys, on the other hand, is affected by the microstructure. It is known that the coercive force of thin sheets of ferro-magnetic material is inversely related to the thickness of the sheet and this has been attributed to stabilisation of the domain structure at surfaces(59). This effect is revealed in cemented carbides by a direct inverse relationship between their coercive force and the mean free path of the binder phase. Thus, for WC-Co alloys, Exner and Fischmeister(55) showed experimentally that:

$$H_c = \frac{73}{\bar{l}}$$  \hspace{1cm} (5)

A similar result was obtained for WC-TiC-Co alloys(41).
1.2. The Microstructure of Cemented Carbides and Factors Affecting It

As well as the decrease in porosity already discussed in section 1.1.1., a number of changes in microstructure are known to occur during liquid-phase sintering. These changes include: the growth of the carbide grains; changes in the carbide grain size distribution; changes in the degree of contact between the carbide grains; and a change towards a characteristic grain shape. At the same time - particularly during sintering in vacuum - there is a loss of metallic binder phase by evaporation.

The extent to which these changes occur can depend on a large number of factors, including the composition of the alloy and the nature of the starting materials, as well as the conditions of sintering.

1.2.1. Carbide Grain Size and Growth

1.2.1.1. Possible Mechanisms of Grain Growth

During liquid-phase sintering, a cemented carbide is essentially a dispersion of solid carbide particles in a molten solution of a fraction of the carbide in the binder metal. The total interface between solid and liquid, and between solid particles in contact, can be reduced by the growth of the particles. Thus the interfacial energies, $\gamma_{sl}$ and $\gamma_{ss}$, act as a driving force for the growth of the carbide grains. A number of mechanisms for growth have been proposed. These are:

i) Solution-reprecipitation\(^{(51)}(60)\).

Growth by a process of dissolution and reprecipitation is able to occur because of the variation of the carbide solubility with particle radius. This process has been treated theoretically, in detail, and is discussed in section 1.2.1.3.

ii) Precipitation of dissolved material onto existing particles during cooling\(^{(51)}(60)\).

Because of the difference in solubility of the carbide in the binder phase when it is liquid and when it is solid, there will almost certainly be some precipitation during cooling after sintering, except, perhaps in cases of rapid quenching. It is considered that precipitation will occur onto existing grains rather than form
new particles$^{(1)}$. There appears to be no specific experimental
evidence for this, but kinetic considerations suggest that it is a
reasonable assumption for the majority of systems. If grain enlarge-
ment by this process does occur, it will depend only on solubilities
at different temperatures and, unlike the solution-reprecipitation
process, will be independent of sintering time. The solubilities of
the carbides in the liquid binder phase are usually relatively low
(Table 3), so that growth by this means would usually be expected to
be quite small. The process has not been accounted for quantitatively
in previous investigations.

iii) Instantaneous coalescence of favourably orientated particles
in contact$^{(51)(39)(42)}$.

There is an extremely small probability that, during sintering,
certain neighbouring grains could have the same lattice orientation.
If they came into contact they would form a single, larger grain.
There is in addition, a similar possibility that low-disorder and
twin-like boundaries could form. This type of growth would be
expected to occur most readily at the start of sintering when, as
discussed in section 1.1.4., the grains are undergoing re-arrange-
ment and move bodily with respect to one another. The process would
also be enhanced considerably if the particles had developed faces
of specific crystallographic habit. The kinetics of such processes
have yet to be examined theoretically and quantitatively.

iv) Coalescence of unfavourably orientated particles by movement
of solid/solid interfaces - i.e. solid state grain growth$^{(39)(61)}$.

The distinction between this type of coalescence and the
instantaneous coalescence discussed above has been emphasised by
Warren$^{(39)}$. It is clear that practically all the grains in contact
in a microstructure have a different spatial crystal-lattice
orientation, so that the coalescence of these would have to occur by
movement of solid/solid interfaces. It was concluded that such a
process probably plays only a small part in determining the grain
growth in most cemented carbides. This can be understood when it is
realised that a considerable proportion of the carbide grain surfaces
are bounded by solid/liquid interfaces. From the point of view of
solid state grain growth, the microstructure may be regarded as a
two-phase alloy in which the solid grain boundaries contain
inclusions of the liquid phase. If the principle of grain growth inhibition by inclusions, proposed by Zener, is applied to such a system, an extremely slow grain growth is predicted, even if the solid/solid boundary has a high intrinsic mobility.

If the mobility of the solid/solid boundary is higher than that of the solid/liquid interface growing by the solution-reprecipitation process, then its movement would be expected to follow and keep up with that of the solid/liquid interface. The growth by solution-reprecipitation would therefore not be seriously affected. If however, the mobility of the solid/solid boundary is lower than that of the solid/liquid interface, then inhibition of the solution-reprecipitation growth would be expected to occur to an extent dependent on the contiguity.

For alloys with very low binder contents or with high contiguity associated with agglomeration of carbide grains, it is possible that solid-state grain growth plays a more dominant part.

There is probably little doubt that all four mechanisms discussed above contribute to carbide grain growth during liquid-phase sintering. A theoretical prediction of the relative importance of each would be very difficult. It is also difficult to draw accurate conclusions from metallographic observation, since individual grains seldom reveal the history of their growth. That coalescence of some sort does occur in certain systems however, is indicated by the presence of spherical inclusions of the binder phase metal, trapped within individual carbide grains (37)(39)(62)(63).

In spite of the many possible mechanisms of growth that have been proposed, only two clearly distinct conceptions of the growth during liquid-phase sintering have so far been developed in experimental and theoretical terms. These are: i) the 'coalescence hypothesis' proposed by Parikh and Humenik (61)(63) and ii) a number of similar theories based on solution-reprecipitation processes. They will be discussed in the following two sections.

1.2.1.2. The Coalescence Hypothesis

The coalescence hypothesis stated that the coarseness of microstructures produced by liquid-phase sintering, increases with decreasing wetting of the solid by the liquid. It was proposed that
this was so because, with decreased wetting, the degree of contact between particles increases, which in turn promotes coalescence.

Experimental verification of the hypothesis was sought by a study of the microstructure of diverse liquid-phase sintered materials and correlation of these with wettability measurements which were made by means of the sessile drop experiment (see section 1.2.6.). Thus the microstructures of WC-Co alloys appeared to be much finer than those of WC-Cu alloys, in which the wettability was much poorer (61)(63). Similarly, additions of Mo to Ni decreased its angle of contact on TiC and at the same time reduced the TiC grain size in TiC-Ni alloys (63).

The hypothesis and the experimental studies upon which it is based, suffer a number of weaknesses. The precise mechanisms of the coalescence were not proposed. The hypothesis was not developed quantitatively; nor were quantitative measurements made of the grain size. In fact, the parameter used to describe the structure coarseness was rather ill-defined, no distinction being drawn between the true grain size and the size of agglomerates of grains.

Although, in the experimental studies carried out, there appeared to be a straightforward relationship between the angle of contact and the wettability in the microstructure, there is no theoretical justification for supposing this to be a general relationship for all systems (see also section 1.2.6.1.).

Remembering the discussion of iv) in the previous section, it seems unlikely that a process of coalescence could lead to substantial increases in true grain size. Nevertheless the coalescence hypothesis might be applicable if a structure-coarseness parameter, related to a mean free path in the carbide phase rather than the grain size, were specified.

1.2.1.3. Theories of Particle Growth by Solution-Reprecipitation in Ideal Systems (Ostwald Ripening)

Unlike the coalescence hypothesis, theories of particle coarsening based on solution-reprecipitation have been developed quantitatively. All the expressions which have been derived to describe growth by such a process, have been based on the assumption that the driving force for the process stems from the particle/matrix interfacial
energy, and also that the solubility of the particle material in the matrix, at the interface, is dependent on the particle radius, in accordance with the Thomson-Freundlich equation:

\[ C_r = C_0 \exp \left( \frac{2 \gamma_{sl} \Omega}{rRT} \right) \]  

where \( C_r \) and \( C_0 \) are the solubilities at interfaces of radius \( r \) and a plane interface respectively; \( \Omega \) is the molar volume of the particle material; and \( \gamma_{sl} \) represents the interfacial energy between particle and matrix (not necessarily liquid in this particular case).

### 1.2.1.3.1. The Theory of Wagner

Three independent, theoretical treatments by Greenwood\(^{64}\), Lifshitz and Slyozov\(^{65}\), and Wagner\(^{66}\), have led to very similar predictions of growth behaviour. Of these, that of Wagner will be examined here as a convenient example.

By considering an array of spherical particles, dispersed in a matrix, and with a distribution of sizes, and by assuming the condition that the distance between the particles was large (i.e. greater than about twice the radius of an average particle), Wagner derived two expressions for the growth of the particles with time. These may be written:

\[ \bar{r}^2 - \bar{r}_o^2 = \frac{6 \gamma_{sl} \Omega^2 C_0}{81 \nu RT} k_r t = K_r t \]  

\[ \bar{r}^3 - \bar{r}_o^3 = \frac{8 \gamma_{sl} \Omega^2 C_0 D}{9 \nu RT} t = K_D t \]  

where \( \bar{r} \) and \( \bar{r}_o \) are the mean particle radii at time \( t \) and at the start of the process, respectively; \( D \) is the coefficient of diffusion of the particle material in the matrix, and \( k_r \) is the reaction rate constant for the transfer of the material across the solid/liquid interface; and \( \nu \) is a constant which depends on the extent of the dissociation, in the solution, of the particle molecules. For a non-dissociating molecule \( \nu = 1 \), and for complete dissociation \( \nu \) is the number of atoms in the molecular formula.

Equation (7) applies when the growth rate is controlled by the transfer of material across the interface, and Equation (8) when it is controlled by diffusion of the material through the matrix.
Wagner showed that, during growth, the size distribution of the particles attains a quasi-stationary form, such that the maximum particle size, \( r_m = 9 \frac{\bar{r}}{b} \) for the interface-controlled growth, and \( r_m = 3 \frac{\bar{r}}{2} \) for the diffusion-controlled growth. Strictly, equations (7) and (8) only apply from the instant these distributions are attained. If the initial distribution is described by a moderately broad Gaussian curve, the time taken to reach the quasi-stationary state is given by:

\[
\tau = \frac{\nu \bar{r}^3 RT}{2 \mathcal{V}_{slD} c_0 \Omega^2} = \frac{4 \bar{r}_o^3}{9 K_D}
\]

for the case of diffusion-control. An analogous equation applies for the case of interface-reaction control.

For long growth times or for large growth rates, \( \bar{r}_o \) becomes small compared with \( \bar{r} \), and equations (7) and (8) may be written:

\[
\bar{r}^2 = K_R t \quad (10)
\]

\[
\bar{r}^3 = K_D t \quad (11)
\]

1.2.1.3.2. The Theory of Exner and Fischmeister

For an interface-reaction controlled growth situation, Exner and Fischmeister (67) derived the equation:

\[
(\bar{D} - \bar{D}_o)^2 = \frac{6 \nu \Omega k_r \mathcal{V}_{slD} c_0}{9 R T} \cdot e^{2\sigma^2}(e^{2\sigma^2} - 1) t
\]

where \( \bar{D} \) and \( \bar{D}_o \) are the mean particle diameters at time \( t \) and the start of the process, respectively. In many respects their derivation was similar to that of Wagner. However, they proposed a log normal particle size distribution with the deviation \( \sigma \), and predicted its effect on the growth rate. Their derivation also involved the assumption that the rate of change of the interfacial area, at time \( t \), is inversely proportional to the relative change in interfacial area that has taken place in that time, i.e.:

\[
\frac{dS}{dt} = \frac{S_o}{S_o - S_t}
\]
It is this assumption— the validity of which is perhaps doubtful—which leads to a form of the rate equation which is fundamentally different to that of the Wagner equations. Equation (7) implies that the rate of growth at any time is inversely proportional to the particle size at that time; whereas Equation (12) implies that the rate of growth is inversely proportional to the change in particle size that has occurred.

1.2.1.3.3. The Herring Scaling Laws

For sintering phenomena in general, Herring derived expressions which predict the degree of material transport as a function of particle size, for different mechanisms of transport. The results of his analysis, if applied to particle growth, may be summarised with the following equations:

For transport by:

- **Viscous flow:**
  \[ \bar{r} - \bar{r}_o = K_v t \]  \hspace{1cm} (13)

- **Evaporation and condensation (i.e. interface-reaction control):**
  \[ \bar{r}^2 - \bar{r}_o^2 = K_I t \]  \hspace{1cm} (14)

- **Volume diffusion:**
  \[ \bar{r}^3 - \bar{r}_o^3 = K_I t \]  \hspace{1cm} (15)

- **Surface migration:**
  \[ \bar{r}^l - \bar{r}_o^l = K_B t \]  \hspace{1cm} (16)

These results are of interest because equations (14) and (15) agree, in form, with the equations (7) and (8) of the Wagner analysis. Equations (13) and (16) describe processes which are unlikely to take place during liquid-phase sintering, although experimental results which fit equation (16) have been observed\(^{39}\)(69)(70) (see also section 1.2.1.5.). Equation (16) can be applied to the growth of grain-boundary precipitates in a solid matrix, where diffusion may occur along the boundaries of the matrix\(^71\).

1.2.1.3.4. The Effect of Temperature on Particle Growth

The analyses of particle growth processes, discussed above, were restricted to isothermal growth. Nevertheless, the effect of temperature, in the ideal situations described by the growth equations, can be predicted by predicting the effect of temperature on the rate constants. The effect is clearly rather complex, since the rate
constants contain a number of temperature dependent parameters. Of these, the diffusion coefficient, $D$, or the interface-reaction rate constant, $r_I$, and the solubility, $C_0$, are probably the most thermally sensitive. Since these three parameters are normally exponential functions of temperature, the variation of the particle growth constant with temperature is often written in the form of an Arrhenius equation:

$$K_D = K_0 \exp(-Q/RT) \quad (17)$$

where $Q$ is often known as the 'activation energy'. This parameter is not however an activation energy in the true physical sense, since it does not refer solely to kinetic factors. Equation (17) should be regarded as a convenient means of expressing the approximate effect of temperature. Although its use has been justified experimentally (section 1.2.1.5.1.), deviations from linearity of the Arrhenius plot are to be expected.

1.2.1.4 Particle Growth in Real Systems

The theoretical treatments of particle growth, presented above in section 1.2.1.3. are valid only for ideal systems, i.e. those systems for which:

a) the particles are spherical,

b) the particle separation is large compared to the particle radius (i.e. no particle interaction),

c) there is no inter-particle contact,

d) the particles are of a non-dissociating compound (or pure element) or a compound which is completely dissociated in the solution.

In real systems, such as cemented carbides, these conditions are seldom all fulfilled. Provided that the deviations from ideality in a given system remain constant throughout the sintering process, the form of the rate equations should remain valid and only the values of the rate constants will be affected, as discussed below.

1.2.1.4.1 The Effect of Particle Shape

Wagner postulated that the effect of grain shape could be allowed for by defining an effective particle radius:

$$r_{eff} = 2(\partial V/ \partial A) \quad (18)$$
where $V$ and $A$ are the volume and surface area of the particle. Thus in equations (7) and (8), $r$ would be replaced by $r_{\text{eff}}$, which for cubic particles is half the cube edge-length. Li and Oriani suggest that the effective radius is the perpendicular distance between the centre and the surface of the particle, averaged in all directions. For a cube with sharp edges and corners, this can also be shown to be half the edge-length. These authors also point out that for non-spherical particles, the effect of orientation on $\gamma_{\text{sl}}$ must also be considered.

1.2.1.4.2. The Effect of Particle Interaction

The derivation of Wagner assumes that the concentration gradient between the particle interface and the liquid matrix extends for a distance equal to the particle radius around the particle. Thus any particle of radius $r$ has an associated 'sphere of influence' of radius $2r$. Should the spheres of influence of different particles overlap, the concentration gradient to and from particles will be increased. For interface-reaction control, this is not expected to affect the flux of material, but for diffusion-controlled growth an increase in the rate is expected.

In cemented carbide microstructures, the average distance between the carbide grains is usually much less than twice the average grain radius, so this type of particle interaction would be expected to occur.

Using a simplified Wagner approach, and by assuming that the average diffusion distance was equal to the mean inter-particle spacing, Sarian and Weart derived an expression which accounts for this interaction:

$$\bar{r}^3 - r_o^3 = k_D k_{\text{i}} t$$  (19)

where $k_{\text{i}} = \frac{4(1 - \alpha)}{3\alpha}$. This would predict an increase in the growth rate at volume fractions of liquid phase of less than about 0.55.

Treating the same situation with a somewhat different approach, Lay obtained the essentially similar equation:

$$\bar{r}^3 = k_D k_{\text{j}} t$$  (20)

where $k_{\text{j}} = \frac{16(1 - \alpha)}{9\alpha}$. The derivation was carried out only for
very small values of $\omega$. The value of $r$ was assumed to be large compared to $r_0$ (cf. equations (10) and (11)).

Equations (19) and (20) do not take into account actual particle contact.

1.2.1.4.3. The Effect of Particle Contact

All cemented carbides examined experimentally, exhibit a certain degree of contiguity. Precise prediction of the effect of this on the solution-reprecipitation growth processes is rather difficult. The following influences of contiguity have been suggested:

i) Contiguity causes a reduction in the interfacial area available for solution and precipitation, thus causing a reduction in growth. This suggestion was modified by pointing out that growth would only be affected if the solid/solid boundary mobility were less than the solid/liquid interface mobility (section 1.2.1.1.). The effect on the observed growth rate could then be rather complex, because the rate of solid/solid boundary motion would be involved.

ii) Contiguity causes an alteration in the radius of curvature of the solid/liquid interfaces. It was first suggested that, for a given volume fraction of liquid phase, contiguity would alter the radius of curvature of the solid/liquid interface in order to maintain the equilibrium dihedral angle. For grains with spherical geometry, the curvature would decrease with an increase in contiguity and therefore the growth rate would also decrease. Stephenson et al. pointed out that contiguity and dihedral angle are not independent at a given volume fraction of liquid, but showed that attainment of equilibrium contiguity did involve modification of the curvature of particles with spherical geometry and with a range of sizes. Similar changes in growth rate to those suggested by Buist et al. were predicted. However, the calculation of the expected curvature for a given contiguity is very complicated and could not be applied to non-spherical particles.

As well as the effects already proposed, it should also be mentioned that, for a fixed volume fraction of liquid, the contiguity will affect the value of the mean free path in the liquid phase (see section 1.2.4.) and so indirectly affect the diffusion gradient as discussed in the previous section.
1.2.1.1. The Effect of Alloy Composition

Three aspects of alloy composition may be distinguished:

1) Non-stoichiometry of the solid (carbide) phase.

The examination, in detail, of the systems, W-C-Co\(^{(4)}\) and Ti-C-Ni\(^{(5)}\), showed that the pseudo-binary between the carbide and the binder phase, in fact only existed between the carbide and a solution of the binder metal richer in transition metal atoms than in carbon atoms. It is also known that the pseudo-binary can exist within a range of carbide composition, without the formation of other phases such as graphite.

This possible variation in atom ratio in the solid and the solution may be expected to affect the values of \(D, C_0\), and \(\gamma_{sl}\). Wagner has suggested that, for a compound \(A_B\), when an excess of \(B\) exists in the solution, the solubility may be defined as the total concentration of the minority component, \(A\), if the formula \(A_B\) is used to define the molar volume, and if \(\gamma\) is taken as unity\(^{(66)}\). In the same situation the diffusion coefficient is taken as that of \(A\) in the liquid.

By postulating that, during the Ostwald ripening of a compound, the composition of the compound must remain constant, Li and Oriani have suggested that there is a composition restraint on the transport of the compound\(^{(73)}\). On this basis they derived an effective diffusion coefficient for the compound \(A_B\):

\[
D_{eff} = \frac{D_A D_B (C_A C_B)^{\frac{1}{2}}}{C_A D_A b^2 + C_B D_B a^2}
\]

(21)

where \(C_A\) and \(C_B\) are the individual concentrations of the constituents in solution. Allowing for the fact that the compound in solution may not be in the stoichiometric ratio, Feingold and Li\(^{(77)}\) derived a similar expression for an effective product of diffusion and solubility:

\[
(CD)_{eff} = \frac{D_A D_B C_A C_B}{b^2 D_A C_A + a^2 D_B C_B}
\]

(22)

Both expressions indicate that the effective parameter is somewhat
lower than that of either of the constituents alone.

There appears to be no direct information, however, on the effect of the deviation from stoichiometry of a compound on its solubility in a liquid; nor on the degree of association of the metal and carbon atoms in liquid metal solutions. The work of Shchetelina suggests that the solubility in the solid state increases markedly with decreasing carbon to transition metal ratio \(^{(78)}\).

ii) Systems of complex composition.

The presence of more than two species of atoms in the solid phase material, as for example in a mixed carbide solid-solution, may be expected to affect the values of \(D\), \(k\), \(C\), and \(\gamma_s\). A theoretical prediction of such effects is extremely difficult. However, if the principle of composition restraint, described above, is applied to such compounds then equations analogous to equations \((21)\) and \((22)\) might be expected to apply. If so, every extra atom species added would be expected to reduce the overall flux of material. Li and Oriani have suggested, furthermore, that increased stability of a compound will tend to reduce its solubility, and that increasing complexity of its composition will inhibit the interface reactions \(^{(73)}\).

In many complex systems there exist more than one solid phase, e.g. two mutually insoluble carbides. Although these can be thought to behave as separate systems in that they both will exhibit growth, they are bound to interact. For example their individual solubilities and diffusivities might be expected to be affected by each others presence. Furthermore, Stephenson and White have suggested, on the basis of experimental observation of multi-component oxide systems, that one species of particles impedes the growth of the other by the formation of contiguous boundaries with them \(^{(43)}\). The reduction in growth of one species increases with the volume fraction of the other (see Figure 8, page 49).

iii) Impurities.

Much of the above discussion of complex systems could be applied to the effect of the presence of impurities. However, impurities have the distinction that they often have a very different chemical nature from the phases that are present by intention. One consequence of this is that they may be very active at the solid/liquid interface. This could, not only reduce the value of \(\gamma_s\) and so reduce the value
of the rate constant, but also inhibit the interface reaction and thereby change the growth process from diffusion to interface-reaction controlled.¹²

1.2.1.5. Experimental Studies of Grain Growth in a Liquid Matrix

Before discussing the reported results of studies of particle growth in a liquid matrix, it is necessary to comment on the interpretation of such results. When measurements of isothermal growth are made, it is usually attempted to fit the results to one of the theoretical growth laws. The most direct method is to test the agreement of experimental and theoretical growth rates. This is usually difficult to accomplish accurately, because of lack of accurate data for the parameters involved in the theoretical rate constants. It is, however, often possible to determine the experimental rate exponent, n, for an equation of the form,

\[ \frac{\bar{r}}{r_0} - \frac{n}{r} = Kt \]

and therefore to obtain an indication of the growth rate process that is operating. Interpretation of results by this means can be uncertain however, because, when growth rates are low, the results sometimes fit more than one equation, within the limits of experimental error.³⁹±⁷

A common method for the determination of n is to plot log \( \bar{r} \) vs log t. If equations (10) or (11) are valid, the plots are straight lines with a slope of 1/n. If, however, \( \bar{r} \) is not much larger than \( r_0 \), the method is not valid and will lead to erroneously high values of n.³⁹(80)

A third method of comparison between theory and experiment was suggested by Wagner.⁶⁶ It involves comparing the experimental particle size distribution with those predicted by theory.⁶⁶(79)(81) Unfortunately it is only possible to carry out a suitable experimental determination of the distribution for particles of certain regular shapes (this is discussed in detail in section 2.5.2.), and so this approach is probably not possible for cemented carbides, although it has been attempted on VC-Co and VC-Ni alloys.⁷⁹(see also section 1.2.1.5.3.). The ratio of the maximum particle diameter to the mean diameter, however, is fairly straightforward to measure.
and can be used to help distinguish between diffusion and interface reaction controlled growth, for ideal growth behaviour (section 1.2.1.3.1.).

A further distinction between diffusion and interface-reaction controlled growth, which it should be possible to observe experimentally, is the different influences of the interparticle spacing (i.e. particle interaction) in the two cases, as discussed in section 1.2.1.4.2.

1.2.1.5.1. General Studies of Particle Growth

Investigations of a large number of systems have confirmed the validity of the form of the Wagner equations, (7) and (8), or (10) and (11); i.e. values of \( n = 2 \) or \( 3 \) are usually observed. Results, which are representative of the main studies so far carried out on cemented carbide systems, are summarised in Table 5. Similar results have been obtained for oxide systems \(^{43}\) \(^{75}\) \(^{76}\) \(^{82}\); all-metal systems such as W-Ni-Cu alloys \(^{70}\) \(^{83}\) and Fe-Cu alloys \(^{84}\); as well as for particle growth in solid matrices \(^{85}\) \(^{86}\) \(^{87}\) \(^{88}\). In certain systems, results have apparently fitted more closely to equation (16) (i.e. \( n = 4 \)). This is to be expected for grain-boundary precipitate particles in a solid matrix \(^{71}\), but has also been observed in liquid matrix systems \(^{39}\) \(^{69}\) \(^{89}\). These examples, however, involve the difficulties in interpretation which were discussed above. For the latter two \(^{69}\) \(^{89}\), \( n \) was determined from log-log plots and might be too high for this reason. Equation (12) was found to be applicable to WC-Co alloys \(^{37}\), but again, the interpretation is uncertain because of a very low growth rate (Table 5).

Where data has been available or could be reasonably guessed at, the calculated values of the theoretical rate constants have shown fair agreement with the experimental values for cases of supposed diffusion-controlled growth \(^{40}\) \(^{74}\).

The effect of temperature has also been investigated in a large number of systems \(^{37}\) \(^{39}\) \(^{40}\) \(^{41}\) \(^{76}\) \(^{79}\) \(^{83}\) \(^{89}\). In those systems which in many respects appeared to exhibit a diffusion-controlled growth behaviour, the value of the 'activation energy', \( Q \), lay between about \( 40 \) and \( 100 \) kcal/mole. These values are probably too high to be explained only by the influence of temperature on \( D \) and \( C \).
TABLE 5 Some examples of experimental studies of carbide grain growth, taken from reported investigations

<table>
<thead>
<tr>
<th>Alloy System</th>
<th>Volume % binder metal</th>
<th>Observed exponent, n, and rate equation</th>
<th>Activation constant, Q kcal/mole</th>
<th>$K_R \text{ cm}^2/\text{sec} \times 10^{12}$</th>
<th>$K_D \text{ cm}^3/\text{sec} \times 10^{12}$</th>
<th>Temperature °C</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC-Co</td>
<td>16.5</td>
<td>2 eq.(12)</td>
<td>142</td>
<td>0.76 0.49</td>
<td>0.00017 0.000114</td>
<td>1420</td>
<td>(37)</td>
</tr>
<tr>
<td>WC-Co</td>
<td>25</td>
<td>n.d.</td>
<td>n.d.</td>
<td>8.0 4.0</td>
<td>0.0022 0.0012</td>
<td>1400</td>
<td>(51)</td>
</tr>
<tr>
<td>WC-Co</td>
<td>25</td>
<td>2.9 eq.(11)</td>
<td>76</td>
<td>uncertain grain size parameter</td>
<td></td>
<td>1300-1600</td>
<td>(69)</td>
</tr>
<tr>
<td>WC-Co</td>
<td>?</td>
<td>3 eq. (8)</td>
<td>85 ± 20</td>
<td>no values given</td>
<td></td>
<td>1300-1600</td>
<td>(91)</td>
</tr>
<tr>
<td>(WC-TiC)-Co</td>
<td>20</td>
<td>n.d.</td>
<td>120</td>
<td>3.0 3.0</td>
<td>0.0008 0.0009</td>
<td>1480</td>
<td>(41)</td>
</tr>
<tr>
<td>TiC-Ni **</td>
<td>30</td>
<td>n.d.</td>
<td>n.d.</td>
<td>350</td>
<td>0.56</td>
<td>1450</td>
<td>(92)</td>
</tr>
<tr>
<td>VC-Co</td>
<td>40</td>
<td>uncertain</td>
<td>26</td>
<td>420 420</td>
<td>1.6 2.0</td>
<td>1500</td>
<td>(79)</td>
</tr>
<tr>
<td>NbC-Co</td>
<td>20</td>
<td>3 eq. (8)</td>
<td>95 ± 15</td>
<td>470 370</td>
<td>0.73 0.74</td>
<td>1420</td>
<td>(39)</td>
</tr>
<tr>
<td>NbC-Ni</td>
<td>20</td>
<td>3 eq. (8)</td>
<td>73 ± 10</td>
<td>220 157</td>
<td>0.245 0.245</td>
<td>1380</td>
<td>(40)</td>
</tr>
<tr>
<td>NbC-Fe</td>
<td>20</td>
<td>3 eq. (8)</td>
<td>73 ± 10</td>
<td>236 175</td>
<td>0.30 0.30</td>
<td>1500</td>
<td>(40)</td>
</tr>
<tr>
<td>NbC-Fe</td>
<td>10 - 20</td>
<td>3 eq. (8)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1700-1900</td>
<td>(74)</td>
</tr>
<tr>
<td>TaC-Co</td>
<td>?</td>
<td>uncertain</td>
<td>n.d.</td>
<td>3.5 7.0</td>
<td>0.0017 0.0042</td>
<td>1450</td>
<td>(79)</td>
</tr>
<tr>
<td>Cr$_3$C$_2$-Ni</td>
<td>20</td>
<td>1.6</td>
<td>-</td>
<td>39</td>
<td>uncertain grain size parameter</td>
<td>1300-1600</td>
<td>(89)</td>
</tr>
</tbody>
</table>

Note: The values of $K_R$ and $K_D$ were calculated from values of $\bar{d}$ and $t$ obtained from the published work, often from diagrams. The value of $K$ given in terms of $\bar{d}$ differs from that given in terms of $\bar{f}$, only by the constant factor 64/27.  ** An infiltrated alloy.
Activation constants, almost low enough to be consistent with a diffusion-controlled process, have been found for VC-Co and VC-Ni alloys. As a result of a study of the grain size distribution in these alloys, however, it was concluded that the growth was interface-reaction controlled.

The value of \( Q \) for interface-reaction controlled growth will depend to a large extent on the activation energy of the reaction involved. Very little is known about such reactions, but studies of the WC-Co system suggest that the activation energy can have values as high as between 100 and 150 kcal/mole.

In Table 5, the results are presented in the form of both \( K_p \) and \( K_R \), calculated from grain sizes at two fixed times, regardless of the apparent growth law. In this way, a direct comparison of the relative rates of growth can be made. It is an indication that the proposed growth law is the correct one, if the experimental rate constant values are independent of the time values.

1.2.1.5.2. Experimental Studies of the Grain Size Distribution

Exner and Fischmeister studied the effect of the carbide powder particle size distribution on the growth of the carbide grains in WC-Co alloys. They found that milled powders exhibited normal size distributions and produced similar distribution widths in the sintered microstructure, regardless of the average particle size. Moreover, the growth rate was not affected. A powder with an artificially broad size distribution, produced by mixing two different powders, showed a greater growth rate during sintering. At the same time the size distribution became narrower, as is predicted by the theory of Wagner.

Exner et al. measured the chord length distributions of the VC grains in WC-Co and WC-Ni alloys and compared these with the chord length distributions that would be generated by the theoretical distributions of the Wagner model. The experimental distributions fitted most closely the theoretical distribution for interface-reaction control, and it was therefore concluded that the growth was interface-reaction controlled. However, the grains in these alloys were not perfectly spherical. Since it seems probable that
that even small deviations in shape can have a marked effect on chord length distributions (section 2.5.2.), this conclusion must be considered with some caution.

1.2.1.5.3. Experimental Studies of the Effect of Non-ideality on Growth

As discussed above, the results of most particle growth studies are treated with reference to the ideal growth equations, even though it is admitted that the ideal conditions are rarely present. Experimental studies of the effects of non-ideal conditions on growth are difficult because the variables such as grain shape, contiguity, and composition, cannot normally be altered independently.

i) Particle interaction.

The distance between particles can be varied by varying the volume fraction of the binder metal, although it is inevitable that the contiguity will also change simultaneously.

Sarian and Weart obtained a value of $n = 3$ for the growth of NbC in Fe, and concluded that the growth was diffusion controlled. However, for alloys containing between 10 and 40 wt% Fe, they found, contrary to expectation, that the growth rate was independent of the liquid-phase content, even though particle interaction would certainly occur at the lower contents.

A small increase in growth rate was observed with decrease in liquid content in oxide systems.

For growth controlled by an interface reaction, the growth rate is expected to be independent of particle interaction and therefore of liquid content (section 1.2.1.1.2.). This has been confirmed in the case of WC-Co alloys.

ii) Particle shape.

No investigation of the effect of particle shape on growth has been attempted. It is probable that particle shape could only be varied by changes in alloy composition (see section 1.2.2.). It has been found, however, that the growth of cubic particles agrees well with the theoretical value of $K_D$ for diffusion-controlled growth in certain systems.

iii) Contiguity.

Buist et al. observed a marked decrease in growth rate in oxide
systems when the contiguity of the solid phase was increased. They explained this in terms of the associated change in the curvature of the solid/liquid interface. However, since the variation in contiguity was a result of changes in the composition of the system, the separate influence of contiguity on growth is uncertain. It is of interest that their observations are contrary to the predictions of the coalescence hypothesis.

iv) Composition.

a) Non-stoichiometry of the solid phase: Some studies of the variation of carbon content, within the pseudo-binary region, have been made on some cemented carbides, in spite of the difficulty of adjusting the carbon content without entering a three-phase region.

In WC-Co alloys Gurland noted a decrease in growth rate with decreasing carbon content. On the other hand a decrease in growth was observed with increasing carbon content in TiC-Ni-Mo alloys. Small increases in the C:Nb ratio in NbC-Co alloys produced a slight decrease in the growth rate. Similarly, Exner et al. observed that additions of Ti or TiO₂ to TiC-Ni alloys caused an increase in grain size, and he attributed this to a reduction in C:Ti ratio in both cases.

b) Complex systems: Experimental results have so far indicated that alloying additions tend to reduce the rate of growth of particles in a liquid matrix, both when the addition forms a separate phase and when it goes into solid (or liquid) solution. Alloys of NbC-Co with additions of up to 5 wt% of TiC or WC, retained a two-phase structure but exhibited a marked reduction in growth rate. It is known qualitatively that small additions (~2 wt%) of TiC, NbC, or TaC form as a second solid phase in WC-Co alloys, at the same time causing a refinement of microstructure.

The effect of two solid phases has been well demonstrated by Stephenson and White for a number of oxide systems and an example is reproduced in Figure 8 (page 49). It can be seen that the growth of one phase decreases continuously as the volume fraction of the other increases.

A further example of refinement of microstructure by alloying, is the addition of Mo or Mo₂C to TiC-Ni alloys. The refinement has been explained in terms of the coalescence hypothesis, as has been
discussed in section 1.2.1.2., but could equally well be accounted for by the solution-reprecipitation processes outlined in section 1.2.1.4.4.; although the interpretation of the effect is complicated by the fact that a Mo-rich layer is known to form on the TiC grains.\(^{(94)}\)

In general, it may be concluded that all the experimental observations on complex systems are qualitatively consistent with the principles discussed in section 1.2.1.4.4.

c) Impurities: The most common impurity in cemented carbides is probably oxygen. No detailed study has been made of its effect on the carbide grain growth. Exner et al. observed that additions of TiO\(_2\) to a TiC-Ni alloy caused an increase in the carbide grain size, and it was suggested that this was because the added oxygen caused a reduction in the carbon content of the carbide.\(^{(79)}\)

Sarian and Weart observed that specimens of NbC-Fe alloys, when sintered on boron nitride substrates, took up the substrate material and that the carbide growth process apparently changed to an interface-reaction controlled process from a diffusion-controlled process which occurred with an inert substrate (NbC or graphite). They concluded that the dissolved boron nitride was active at the solid/liquid interface and formed an interfacial layer.\(^{(74)}\)

The addition of up to 3.75 wt% NbB\(_2\) to NbC-Co alloys did not appreciably affect the carbide grain size, but changed the form of the growth from that described by equation (8) (i.e. diffusion control), to that described by equation (16), which indicates diffusion along an interface. The growth also agreed fairly well, however, with the form of equation (12)\(^{(39)}\).

1.2.2. The Carbide Grain Shape

1.2.2.1. Theoretical Predictions of Grain Shape

Because of the relatively high mobility of the solid/liquid interface and because of the lack of rigidity of the liquid, particles growing in a liquid are usually able to take up a shape consistent with minimum interfacial free energy. For an isotropic material, this shape is spherical. For anisotropic materials, the effect of anisotropy of interfacial energy on the shape is predicted by the theorem of Wulff\(^{(95)}\), as has been discussed by Herring\(^{(96)}\). In practice, in
cemented carbides the equilibrium shape is modified by inter-particle contact, but can normally still be recognised.

Investigations of the systems: TiC-Co(36)(79), TiC-Ni(92)(97), NbC-Co(39), NbC-Ni(100), NbC-Fe(100), TaC-Co(79) and TaC-Ni(79), indicate that the grains of cubic carbides take up a cubic shape, presumably due to the development of the {100} crystallographic planes. As an exception to this, the grains in the alloys WC-Fe and WC-Ni were observed to be nearly spherical(79). The many investigations of WC-Co alloys indicate that the WC grains have a triangular prismatic shape. This has been confirmed by studying single WC crystals leached out from a matrix(99)(100).

The Wulff theorem predicts that a sharp cornered cubic shape will occur only if the interfacial energy on the {100} planes is less than \( \frac{1}{\sqrt{3}} \) of the interfacial energy of the other planes (it being assumed that there are no other low energy planes). As the ratio of the energies increases from this value, rounding of the cube corners and edges occurs, until a spherical shape is attained at an energy ratio of unity. Warren has attempted to describe the effect of the energy ratio on the degree of rounding of a cubic grain in quantitative terms. The result of his analysis suggested that the shape changes from a near-spherical to a near-cubic appearance over a very narrow range of energy ratio(39). However, the shapes that were assumed to occur between the pure cube and the pure sphere, in his model, were not consistent with the Wulff theorem, so that the accuracy of the conclusions drawn from the analysis is somewhat uncertain.

1.2.2.2. Experimental Studies of Carbide Grain Shape

The sensitivity of the shape of cubic carbide grains to small changes in the ratio of the interfacial energies is suggested by experimental observations. Thus, in TiC-Co and TiC-Ni alloys the cubic shape of the TiC grains has been found to be very sensitive to the presence of oxygen, but the exact influence of the impurity is somewhat unclear. Whalen and Humenik found that the presence of oxygen caused rounding of otherwise angular cubic grains, or caused the development of faces other than the (100) faces(97). Exner et al., however, observed that the presence of oxygen or a reduction in carbon content increased the angularity of the grains(79). A similar
sensitivity of shape was found in NbC-Co alloys when small additions of TiC, WC or NbB₂ were made, and in NbC-Fe alloys when traces of boron nitride were present.

The cubic shape of these carbides is also sensitive to temperature. The grains in NbC-Co, NbC-Ni, and NbC-Fe alloys were found to become more rounded with increasing sintering temperature. For NbC in Fe it was found that the grains changed from near-cubic to near-spherical over a quite narrow temperature range, at about 1725°C.

Another observation in the study of the NbC alloys was that, although the majority of grains were cubic, a proportion of the smaller ones were more nearly spherical. One reason for this is that the plane of the microsection passes through the rounded corners of some of the grains. However, Sarian and Weart also postulated that the shape of the smaller grains, which according to the Wagner model are dissolving, is dictated more by kinetic effects than by interfacial energies, and is therefore more rounded.

1.2.3. **Inter-particle Contact - Contiguity, Continuity, and Dihedral Angle**

1.2.3.1. **Theoretical Predictions**

Until quite recently there was a body of opinion which considered that the carbide grains in cemented carbides remain completely surrounded by the binder phase during sintering and even in the subsequent room temperature condition. This opinion was partly based on observations of the mechanical behaviour of the alloys, and perhaps also on the requirements of the Kingery model of densification (section 1.1.4.2.). However, metallographic observations have invariably indicated that, at room temperature at least, a considerable proportion of contiguous boundaries exist, and that the absence of even an extremely thin cobalt layer in contiguous boundaries was demonstrated.

The circumstances at the temperature of sintering are more difficult to determine. Nevertheless, it may be stated that two grain
interfaces in contact will become contiguous if:

\[ \gamma_{ss} < 2 \gamma_{sl} \]  

It is almost certain that this condition will be fulfilled between grains of certain relative orientations \((25)(27)(39)\). Furthermore, as was pointed out in section 1.1.4.2., the presence of contiguous boundaries need not be inconsistent with mechanisms of shrinkage of the kind proposed by Kingery.

1) Theoretical predictions of contiguity.

The degree of contiguity of particles of a phase in a microstructure depends on two main factors:

a) The degree of 'coincidence' of the particles in space, i.e. the frequency of contact. This is determined by statistical probability, and will be affected by the volume fraction of the phase \((l7)\) and the shape of the particles (e.g. spherical particles will be less likely to touch than particles of other shapes) \((39)\).

Particles with flat surfaces are also expected to develop higher contiguity because, as discussed in section 1.1.4.1., the forces that occur during the re-arrangement process of densification tend to bring such faces together.

b) The relative values of the interfacial energies, \(\gamma_{sl}\) and \(\gamma_{ss}\), as is indicated by the relationship \((23)\).

Bearing in mind these two main factors, it is possible to make certain qualitative predictions. With increasing volume fraction of binder (or liquid) phase there will be a continuous decrease in contiguity, from \(G = 1 \) at \( \alpha = 0 \), to \( G = 0 \) at \( \alpha = 1 \). The way that \( G \) changes with \( \alpha \) between these limits is expected to depend on the relative values of \(\gamma_{sl}\) and \(\gamma_{ss}\) \((39)\). A more precise or quantitative prediction of contiguity for the majority of real systems would be an extremely complex problem because of the non-uniformity of the particle size, the anisotropy of the interfacial energies, and because of the difficulty of dealing mathematically with all but the simplest of particle shapes \((104)\).

By considering a regular array of uniformly-sized, contiguous particles of spherical geometry, Stephenson and White derived an expression for the total interfacial energy of the system as a function of the ratio of \(\gamma_{sl}\) and \(\gamma_{ss}\), the degree of contact, and the
number of inter-particle contacts. By using this expression it is possible to derive that contiguity which gives the minimum total energy at a given \( \gamma_{sl} : \gamma_{ss} \) ratio \(^{(43)}\). However, since the equilibrium configuration of particles requires a unique value of volume fraction, the effect of volume fraction is not accounted for in this derivation.

The treatment of Stephenson and White does demonstrate the plausibility of the concept of an equilibrium value of contiguity for a given system. No predictions have yet been made of how the contiguity moves towards this equilibrium value during sintering. It is reasonable to expect that the rate at which the equilibrium is reached depends on rates of material transport.

ii) Theoretical predictions of continuity.

The continuity of the carbide phase, like the contiguity, is dependent on the statistical probability of impingement of the particles \(^{(47)}\) and consequently on the volume fraction and grain shape. The interfacial energies, however, will affect the continuity only by determining whether or not impinging particles form a contact, but not by determining the area of contact. Consequently, the relationship between contiguity and continuity is not necessarily the same in different systems.

Gurland was able to predict, with the aid of probability theory, the number of inter-particle contacts and the probability of complete continuity as a function of the volume fraction, in a system of spheres. The critical number of contacts per particle, required to achieve complete continuity, was determined as 1.3 to 1.5 \(^{(48)}\). This was confirmed by measurements of the microstructural properties and electrical resistivity of a composite of silver spheres in bakelite \(^{(47)}\).

iii) Predictions of Dihedral Angle.

Like contiguity, the dihedral angle between carbide grains is a function of the ratio of \( \gamma_{sl} \) and \( \gamma_{ss} \), thus:

\[
\cos \frac{\theta}{2} = \frac{\gamma_{ss}}{2 \gamma_{sl}} \tag{24}
\]

Unlike contiguity, the dihedral angle is independent of the volume fraction of the binder phase, and in microstructures with a low binder content, the grain shape can change to allow the equilibrium
FIGURE 8  The effect of the presence of two solid phases on the grain growth of each in liquid iron oxide – after Stephenson and White\textsuperscript{(13)}.

FIGURE 9  The effect of the cobalt content on the carbide contiguity of certain cemented carbides.
angle to form. For grains with anisotropy of interfacial energy, the
dihedral angle is no longer a function of two unique energy values,
and equation (24) no longer applies (43).

It follows from the discussion of the above three parameters that
the effect of alloy composition, alloying additions and impurities, on
the degree of particle contact will be determined mainly by their
effect on the relative values of the interfacial energies in the
system. Such effects can be quite marked, since even small quantities
of additions can be interfacially active.

1.2.3.2. Experimental Studies of Inter-particle Contact

It should be pointed out that all experimental results, and the
conclusions drawn from them, refer to the microstructure at room
temperature.

i) The effect of binder content, α.

Reported experimental results, indicating the effect of binder
phase content on the contiguity of cemented carbides, are summarised
in Figure 9 (page 49). The expected effect of α on G is observed.
Contiguitics of other carbide systems at fixed values of α are given
in Table 6.

<table>
<thead>
<tr>
<th>TABLE 6 The contiguities of some cemented carbides</th>
</tr>
</thead>
<tbody>
<tr>
<td>System</td>
</tr>
<tr>
<td>------------</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>WC-Co</td>
</tr>
<tr>
<td>WC-Co</td>
</tr>
<tr>
<td>(WC-TiC)Co</td>
</tr>
<tr>
<td>TiC-Co</td>
</tr>
<tr>
<td>VC-Co</td>
</tr>
<tr>
<td>TaC-Co</td>
</tr>
<tr>
<td>NbC-Co</td>
</tr>
<tr>
<td>NbC-Ni</td>
</tr>
<tr>
<td>NbC-Fe</td>
</tr>
</tbody>
</table>
The precise effect of binder content on the continuity of the carbide seems to be unclear. Although it is certain that increasing \( x \) will decrease the continuity, the question of whether or not the carbide phase forms a continuous skeleton at a particular binder content, has long been a matter of controversy. This is bound up with the controversy over the existence of contiguity already mentioned in section 1.2.3.1. Metallographic observation of alloys with commercial compositions suggests that the carbide is completely continuous, at the cobalt contents normally found in such alloys, although this is difficult to confirm quantitatively for three dimensions. Early experiments in which the cobalt was leached out of sintered WC-Co alloys do suggest a continuous skeleton for alloys with up to about 10 vol\% Co.

Gurland studied the effect of the cobalt content of WC-Co and TiC-Co alloys on the number of contacts per grain, \( \overline{N}_c \) (see section 1.3.3.1.vii), and found that, as expected, \( \overline{N}_c \) fell with increasing \( x \). At about 20 vol\% Co the value of \( \overline{N}_c \) was about 5 for WC and 7 for TiC. His later measurements of electrical resistivity on dispersions of silver spheres in bakelite, demonstrated that complete continuity of the particles occurred at between 1.3 and 1.5 contacts per particle, which corresponded to a volume fraction of bakelite of 0.62, and a contiguity of the particles of about 0.15. This would strongly suggest the carbide phase, in the alloys that he studied, were completely continuous, even allowing for the uncertainty in their \( \overline{N}_c \) values.

ii) The effects of sintering time and temperature.

Reported results of the effect of sintering time on contiguity are somewhat conflicting. Investigations of WC-Co and TiC-Co alloys by Gurland, suggested that contiguity increases with sintering time; e.g. for a WC-Co alloy containing about 37 vol\% Co, sintered at 1100°C, the contiguity increased from about 0.25 at the start of sintering, to about 0.47 after 7 hours. Conversely, the results of Exner and Fischmeister indicated a fall in contiguity with sintering time for WC-Co alloys; thus for an alloy containing about 17 vol\% Co, sintered at 1120°C, the contiguity decreased from 0.195 after 10 minutes to 0.122 after 10 hours, and continued to fall slightly during longer sintering times. Exner and Fischmeister attributed the difference in findings to the fact that they had used electron microscopy and
achieved better resolution of the microstructure*(38)*

The investigations of NbC-Co alloys indicated a similar time
dependence to that found by Exner and Fischmeister, i.e. an initial
rapid decrease in contiguity, followed by a slower decrease towards a
constant value*(39)*. Stjernberg, also using electron microscopy,
observed decreases in contiguity at prolonged sintering times in
(WC-TiC)-Co alloys although the contiguity in some cases increased
slightly during the early stages of sintering. It has to be assumed
that in all these studies the binder content remained constant during
sintering. For the NbC-Co alloys the contiguity values were in fact
corrected to allow for changes that occurred in the binder content*(39)*
(see section 1.2.5.).

Only one study has been made of the effect of sintering time on
the dihedral angle during liquid-phase sintering. For W-Cu-Ni alloys
it was found that the dihedral angle increased towards a constant
value as sintering progressed*(70)*.

In all studies carried out so far on the effect of the temperature
of sintering on the contiguity, it has been observed that there is a
small decrease in contiguity with increase in temperature*(37)(39)(40)
(41)(105)*. This is, no doubt, associated with changes in interfacial
energies. It has also been suggested that the rate of approach to a
constant value would be expected to increase with temperature*(39)*.

In conclusion, it may be stated that all the studies of the
effects of sintering conditions on particle contact indicate that
there is a tendency for the microstructure to take up an equilibrium
configuration. The apparent conflict in experimental observations of
the way that contiguity changes during sintering might simply be due
to differences in the degree of particle contact at the onset of
sintering. The initial degree of contact would be expected to depend
on the pre-sintering treatment and the duration of heating-up prior
to sintering, about which no information was given in the cited works.

iii) The effects of alloy composition.

The addition of 5 wt% TiC to a NbC-Co alloy containing about
20 vol% Co caused a marked increase in the contiguity*(39)*. This might
be explained in terms of a change in the relative values of \( \gamma_{gl} \) and
\( \gamma_{gg} \), caused by the TiC. It was also noted, however, that there was an
associated change in grain shape, from rounded cubes to sharp-edged
cubes, which would also be expected to increase the contiguity (39).

Another notable example of the effect of alloy composition is the addition of Mo to TiC-Ni alloys, already mentioned in section 1.2.1. Qualitative observations indicated that the addition improved the wetting in the microstructure of the TiC grains by the binder metal, i.e. that it caused a reduction in contiguity and dihedral angle. This effect might be associated with the formation of the Mo-rich layer on the outside of the TiC grains, which has been observed (94) and which might be expected to alter the interfacial energy relationships in the system.

1.2.4 The Mean Free Path of the Binder Phase

The mean free path of the binder phase - which, as discussed in section 1.1.6., is an important parameter from the point of view of the mechanical and physical properties of cemented carbides - is fixed by the other microstructural parameters, viz: binder phase content, carbide grain size, and contiguity. It can in fact be shown that:

\[ \bar{\ell} = \frac{\alpha \bar{d}}{(1 - \alpha)(1 - \xi)} \]  

(25)

Thus, the value of \( \bar{\ell} \) for a given set of conditions, can be predicted if the parameters \( \alpha \), \( \xi \), and \( \bar{d} \) can be predicted. For example, if the volume fraction of the liquid phase and the contiguity of an alloy remain constant during sintering, then \( \bar{\ell} \) will be directly proportion-al to the carbide grain size, and will obey a similar growth law (39). In practice, both \( \alpha \) and \( \xi \) tend to decrease to some extent during sintering (section 1.2.5. and 1.2.3.2.), but for values of \( \alpha \) usually present in cemented carbides, these two effects cancel out to some extent.

The approximate proportionality between \( \bar{\ell} \) and \( \bar{d} \) that is predicted has been confirmed for growth in WC-Co alloys (37) and NbC-Co alloys (39).

1.2.5. The Volume Fraction of the Binder and Liquid Phases

When considering processes of liquid-phase sintering through studies of room-temperature microstructures, the differences between the binder phase at room temperature, and the liquid phase at the
sintering temperature, should always be remembered. The most important difference is that during sintering, the liquid binder contains a higher content of dissolved carbide than the binder at room temperature. As well as altering the chemical nature of the binder phase, this also means that the volume fraction of the liquid will be greater than that of the binder phase at room temperature. As a result, parameters such as contiguity will also be affected.

Once the equilibrium solubility has been attained, after the sintering temperature has been reached, it is to be expected that the volume of the binder phase will remain almost constant. (It should, in fact, fall slightly since the overall solubility decreases with increasing grain size). Increasing the sintering temperature will, of course, cause an increase in the liquid content by increasing the solubility.

In practice, because of evaporation, the volume fraction of the liquid phase does not stay constant. Rüdiger and Rottger measured the evaporation rate of cobalt from a number of commercial cemented carbides, as a function of temperature and pressure in a vacuum (down to $10^{-4}$ torr). As an example of this study, a WC-Co alloy which contained 30 vol% Co, lost $6.8 \times 10^{-6}$ gm/cm$^2$ sec at 1400°C, and $2.9 \times 10^{-5}$ gm/cm$^2$ sec at 1500°C, in a vacuum of $10^{-4}$ torr. The evaporation was eventually inhibited by the formation of a liquid-free layer of WC at the surface. Such protective layers did not form, however, in alloys which contained TiC.

A similar loss of binder phase was observed in NbC-Co, NbC-Ni, and NbC-Fe alloys during vacuum sintering. The observed losses are such that the change in $\alpha$ during sintering must be taken into account when other microstructural parameters are being measured. The change in $\alpha$ was apparently not measured in many of the investigations which have been discussed in earlier sections. Most of these investigations were carried out on specimens sintered in hydrogen, in which evaporation would not be expected to be so rapid. Nevertheless, it is possible that this effect might have led to some misleading observations of, for example, contiguity and density changes.
1.2.6. Physico-chemical Studies and Data Relevant to Studies of Cemented Carbide Microstructures

1.2.6.1. Surface and Interfacial Energies - The Sessile Drop

It has become apparent in the preceding sections, to what a large extent the appearance of the microstructure of cemented carbides is influenced by the interfacial energies, $\gamma_s$ and $\gamma_{ss}$. Similarly, the values of the surface energy of the liquid phase, and the angle of contact of the liquid on the solid, have been shown to be of importance for the densification during liquid-phase sintering. The measurements that have been made of these parameters will now be discussed.

1) The liquid surface energy, $\gamma_{lv}$.

The surface energy of liquid metals can be measured quite accurately by a number of methods, which all involve the measurement of the shape of a drop of the liquid\(^{(107)}\). The main source of error in such measurements is caused by the presence of trace impurities which are surface active, such as oxygen, sulphur, and other low melting-point elements, and which can reduce drastically the measured surface energy\(^{(107)}\). Values of $\gamma_{lv}$ for cobalt, nickel and iron, are listed in Table 7.

For cemented carbides, the relevant values of $\gamma_{lv}$ are those of the metal containing a proportion of dissolved carbide. There is much evidence to indicate that the effect of dissolved carbides on the surface energy of these metals is slight\(^{(108)}\)\(^{(109)}\)\(^{(110)}\), although they may make them more susceptible to oxidation\(^{(110)}\).

<table>
<thead>
<tr>
<th>Metal</th>
<th>$\gamma_{lv}$ ergs/cm(^2) at temperature T°C</th>
<th>M. Pt., T(_m)°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>1880 - 0.4(T - T(_m))</td>
<td>1495</td>
</tr>
<tr>
<td>Ni</td>
<td>1780 - 0.36(T - T(_m))</td>
<td>1453</td>
</tr>
<tr>
<td>Fe</td>
<td>1880 - 0.34(T - T(_m))</td>
<td>1539</td>
</tr>
</tbody>
</table>

TABLE 7: The surface energies of liquid Co, Ni, and Fe
(determined by B.C. Allen\(^{(111)}\))
ii) The angle of contact, $\theta$, (and eutectic temperature, $T_e$).

The angle of contact of a liquid-metal on a solid carbide can be measured quite conveniently by the sessile-drop technique, in which a drop of the proposed binder metal is melted on the polished surface of a specimen of the proposed carbide\(^{(27)(112)}\). This technique is very useful since it not only yields a value of $\theta$ and information about the interfacial energies of the system, but also allows a study of the solid/liquid interface by metallographic sectioning after the experiment. Furthermore, if the system can be viewed during the experiment, an approximate value for the eutectic temperature of the system can be obtained\(^{(27)(112)}\).

A schematic diagram of the sessile-drop test is shown in Figure 10 (page 71), in which the solid/liquid interface is shown as flat. The interface usually remains flat when the solubility of the solid in the liquid is low. To a close approximation\(^{(112)}\), the surface and interfacial energies in the sessile-drop system are related by the equation:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \quad (26)$$

The value of $\theta$ is sometimes used as an indication of the degree of wetting (and therefore the contiguity) that can be expected to occur in a pore-free, liquid-phase sintered microstructure\(^{(61)(63)}\). Since the contiguity is determined solely by the relative values of $\gamma_{sl}$ and $\gamma_{ss}$, this is strictly not justified. However, the value of $\gamma_{lv} \cos \theta$ is an indication of the strength of binding between the solid and the liquid and so might perhaps be used as a guide to the wetting in the microstructure\(^{(27)}\). Some values of $\theta$, $T_e$, and $\gamma_{lv} \cos \theta$, for liquid cobalt on single and mixed carbides are given in Table 8.

iii) The interfacial energies, $\gamma_{sl}$ and $\gamma_{ss}$.

The measurement of the interfacial energies is difficult. One possible method is that known as the method of multiphase equilibrium, which is also used to measure the surface energy of solids\(^{(114)(115)}\). The method is described in greater detail in section 1.3.4. It involves measuring the relationship between $\gamma_{sv}$, $\gamma_{sl}$, and $\gamma_{lv}$ by the sessile-drop method; the ratio of $\gamma_{ss}$ to $\gamma_{sv}$ by grain-boundary grooving; and the ratio of $\gamma_{ss}$ to $\gamma_{sl}$ by the measurement of the
### Table 8: The wetting of carbides by liquid cobalt in vacuum; and relevant surface energies

<table>
<thead>
<tr>
<th>System</th>
<th>Temperature of experiment, °C</th>
<th>Eutectic temp. $T_e$ °C</th>
<th>Angle, $\theta$° (± 2°)</th>
<th>$\gamma_{lv}$ ergs/cm²</th>
<th>$\gamma_{lv} \cos \theta$ ref.(111) ergs/cm²</th>
<th>$\gamma_{sv}$ theoretical ergs/cm² (132)</th>
<th>Source ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC-Co</td>
<td>1420</td>
<td>1380</td>
<td>25</td>
<td>1910</td>
<td>1731</td>
<td>2755</td>
<td>(112)</td>
</tr>
<tr>
<td>ZrC-Co</td>
<td>1410</td>
<td>1380</td>
<td>36</td>
<td>1545</td>
<td>2660</td>
<td></td>
<td>(112)</td>
</tr>
<tr>
<td>HfC-Co</td>
<td>1410</td>
<td>1380</td>
<td>40</td>
<td>1463</td>
<td>2955</td>
<td></td>
<td>(112)</td>
</tr>
<tr>
<td>WC$_{0.88}$-Co</td>
<td></td>
<td>1350</td>
<td>13</td>
<td>1861</td>
<td>2960</td>
<td></td>
<td>(112)</td>
</tr>
<tr>
<td>NbC-Co</td>
<td></td>
<td>1400</td>
<td>14</td>
<td>1853</td>
<td>3010</td>
<td></td>
<td>(112)</td>
</tr>
<tr>
<td>TaC-Co</td>
<td></td>
<td>1400</td>
<td>13</td>
<td>1861</td>
<td>3170</td>
<td></td>
<td>(112)</td>
</tr>
<tr>
<td>Mo$_2$C-Co</td>
<td></td>
<td>1310</td>
<td>0</td>
<td>1910</td>
<td>-</td>
<td></td>
<td>(112)</td>
</tr>
<tr>
<td>WC-Co</td>
<td></td>
<td>(1390)</td>
<td>0</td>
<td>1910</td>
<td>-</td>
<td></td>
<td>(112)</td>
</tr>
<tr>
<td>NbC-Co</td>
<td>1400</td>
<td>1390</td>
<td>12</td>
<td>1918</td>
<td>1876</td>
<td></td>
<td>(113)</td>
</tr>
<tr>
<td>NbC-Co</td>
<td>1420</td>
<td>&quot;</td>
<td>12</td>
<td>1910</td>
<td>1868</td>
<td></td>
<td>(113)</td>
</tr>
<tr>
<td>NbC-Co</td>
<td>1450</td>
<td>&quot;</td>
<td>10</td>
<td>1898</td>
<td>1869</td>
<td></td>
<td>(113)</td>
</tr>
<tr>
<td>NbC-Co</td>
<td>1470</td>
<td>&quot;</td>
<td>12</td>
<td>1886</td>
<td>1845</td>
<td></td>
<td>(113)</td>
</tr>
<tr>
<td>(WC-30TiC)$_{Co}$</td>
<td>1420</td>
<td>n.d.</td>
<td>17</td>
<td>1910</td>
<td>1827</td>
<td></td>
<td>(112)</td>
</tr>
<tr>
<td>(WC-50TiC)$_{Co}$</td>
<td>1420</td>
<td>n.d.</td>
<td>21</td>
<td>1910</td>
<td>1783</td>
<td></td>
<td>(112)</td>
</tr>
<tr>
<td>(WC-50TiC)$_{Co}$</td>
<td>1420</td>
<td>1390</td>
<td>24$^{1/2}$</td>
<td>1910</td>
<td>1738</td>
<td></td>
<td>(27)</td>
</tr>
</tbody>
</table>

*Carbide composition given in wt%
dihedral angle in a microstructure. With these three relationships it is possible to determine $\gamma_{sS}$, $\gamma_{sl}$, and $\gamma_{sv}$, if $\gamma_{lv}$ is known.

This method has yet to be applied to cemented carbide systems, although Hodkin et al. have confirmed by the grain-boundary grooving experiment that, for uranium carbide, the ratio $\gamma_{sS}:\gamma_{sv}$ lies between 0.37 and 0.41, as is the case for many cubic metals (116). They also measured the ratio, $\gamma_{sl}:\gamma_{sS}$ in the U-UO system by measurement of dihedral angles (117).

Theoretical values of $\gamma_{sv}$ for carbides, derived by Kislyi and Kuzenkova on the assumption that the surface energy originates mainly from unsatisfied carbon bonds at the surface, are also included in Table 8.

1.2.6.2. The Solubility of the Carbide in the Binder Metal

The solubilities of carbides in liquid metals can be determined by the standard techniques of phase equilibrium determination (4)(5)(7). However, except for the investigations of the systems W-C-Co, Ti-C-Ni, and Ti-C-Fe, already mentioned in section 1.1.2., solubility data is very sparse. There is slightly more information on the solubility of carbides in solid metals close to the eutectic temperature. It has been found that the solubility in the solid state increases markedly with decrease in the carbon:transition metal atom ratio (5)(78). Available data for the solubilities of carbides in cobalt is given in Table 9.

1.2.6.3. The Diffusion Coefficient, $D$, and Reaction Rate Constant, $k_r$

Methods of measuring diffusion in liquid metals have been reviewed by Edwards et al. (121).

No information exists on the diffusion of carbides, as such, in liquid metals. However, it was seen in section 1.2.1.4.4. that the diffusion of a compound may be related to the diffusion of its constituent elements. Furthermore, it is known from the studies of diffusion in liquid metals in general, that diffusion coefficients vary comparatively little from system to system, and that activation energies for liquid-state diffusion nearly all lie within the range, 5 - 20 kcal/mole (72)(121)(122). Therefore, some knowledge of the diffusion of carbides can be gained from results of diffusion studies of carbon and the transition metals alone in the relevant liquids.
### TABLE 9 Solubilities of carbides in cobalt

<table>
<thead>
<tr>
<th>Carbide</th>
<th>Temp. °C</th>
<th>Solubility wt%</th>
<th>Remarks</th>
<th>Source Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC</td>
<td>1330</td>
<td>0.25</td>
<td></td>
<td>78</td>
</tr>
<tr>
<td>NbC</td>
<td>1330</td>
<td>0.5</td>
<td></td>
<td>78</td>
</tr>
<tr>
<td>TaC</td>
<td>1330</td>
<td>0.8</td>
<td></td>
<td>78</td>
</tr>
<tr>
<td>Mo$_2$C</td>
<td>1330</td>
<td>4.6</td>
<td></td>
<td>78</td>
</tr>
<tr>
<td>WC</td>
<td>1330</td>
<td>9.6</td>
<td></td>
<td>78</td>
</tr>
<tr>
<td>TiC</td>
<td>1250</td>
<td>1.0</td>
<td></td>
<td>118</td>
</tr>
<tr>
<td>VC$_3$</td>
<td>1250</td>
<td>6.0</td>
<td></td>
<td>118</td>
</tr>
<tr>
<td>NbC</td>
<td>1250</td>
<td>5.0</td>
<td></td>
<td>118</td>
</tr>
<tr>
<td>TaC</td>
<td>1250</td>
<td>3.0</td>
<td></td>
<td>118</td>
</tr>
<tr>
<td>Mo$_2$C</td>
<td>1250</td>
<td>13.0</td>
<td></td>
<td>118</td>
</tr>
<tr>
<td>WC</td>
<td>1250</td>
<td>22.0</td>
<td></td>
<td>118</td>
</tr>
<tr>
<td>TiC</td>
<td>1280</td>
<td>1.0</td>
<td></td>
<td>119</td>
</tr>
<tr>
<td>WC</td>
<td>1280</td>
<td>3.0</td>
<td></td>
<td>119</td>
</tr>
<tr>
<td>WC-50TiC</td>
<td>1250</td>
<td>2.0</td>
<td></td>
<td>118</td>
</tr>
<tr>
<td>WC-50TiC</td>
<td>1280</td>
<td>2.0</td>
<td></td>
<td>119</td>
</tr>
<tr>
<td>WC-30TiC</td>
<td>1330</td>
<td>0.5</td>
<td>Free C present</td>
<td>78</td>
</tr>
<tr>
<td>TiC</td>
<td>$T_e$, 1360</td>
<td>10</td>
<td>Eutectic liquid</td>
<td>120</td>
</tr>
<tr>
<td>VC</td>
<td>$T_e$, ~12</td>
<td></td>
<td>Eutectic liquid</td>
<td>120</td>
</tr>
<tr>
<td>NbC</td>
<td>$T_e$, 11</td>
<td></td>
<td>Eutectic liquid</td>
<td>120</td>
</tr>
<tr>
<td>TaC</td>
<td>1420</td>
<td>14.5</td>
<td>Liquid</td>
<td>10</td>
</tr>
</tbody>
</table>

*Probably non-stoichiometric VC
The diffusion of carbon in liquid iron has been measured by a number of investigators\(^{123}(124)(125)(126)(127)\). The most probable value of \(D\) for carbon in iron would appear to lie between about \(7 \times 10^{-5}\) and \(10^{-4}\) \(\text{cm}^2/\text{sec}\), for temperatures between 1400°C and 1550°C. The diffusion rate falls slightly with increasing dissolved carbon content. The activation energy lies between about 8 and 16 kcal/mole.

Available data for the diffusion of some group IV and V transition metals in liquid iron is summarised in Table 10.

The only investigation that has been carried out on the dissolution kinetics of a carbide in a liquid metal is that of Skolnick who studied the dissolution of WC in cobalt\(^{(90)}\). He found the dissolution rate was controlled by an interfacial reaction. The activation energy for the reaction was 175 ± 4 kcal/mole, and the rate constant was \(3 \times 10^{-4}\) \(\text{cm/sec}\) at 1450°C.

1.2.6.4. Grain Growth and Diffusion in Solid Carbides

In view of the possible part played by contiguous carbide boundaries, and because of its general relevance, the process of diffusion in solid carbides should be considered.

Information on solid state grain growth in carbides is surprisingly sparse. For NbC\(_{0.8}\), Ordanyan and Avgustnik\(^{(130)}\) obtained experimentally the following relationship for the grain growth:

\[
\frac{d^2}{dt^2} = 1.78 \times 10^8 \exp(-65,500/RT) t=30 \text{ min.}
\]

In hot-pressed carbides, Samsonov and Boschko\(^{(131)}\) found that the activation energy for growth increased with carbon content for:

- TiC (Q = 25 - 35 kcal/mole);
- ZrC (45 - 55);
- and NbC (60 - 70).

There exists considerable information on the self-diffusion of carbon in carbides. Approximate 'likely' values, estimated from this information are given in Table 11. In general, the activation energy falls and the diffusion rate increases with decreasing carbon content.

For the diffusion of Ti in TiC, Sarian obtained a value for Q of 176,4 kcal/mole, and rates of diffusion lower than that of carbon by a factor of approximately \(10^4\) \(^{(133)}\). Furthermore, the diffusion was not dependent on the deviation from stoichiometry of the carbide. Sarian concluded that the carbon and metal atoms diffuse independently.
### TABLE 10  The diffusion of some metals in liquid iron

<table>
<thead>
<tr>
<th>Metal</th>
<th>Temperature°C</th>
<th>( D, \text{cm}^2/\text{sec} )</th>
<th>( Q, \text{kcal/mole} )</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>1440</td>
<td>( 5.0 \times 10^{-5} )</td>
<td>6.4</td>
<td>0.6% Ti in C-saturated Fe</td>
<td>124</td>
</tr>
<tr>
<td>Ti</td>
<td>1450</td>
<td>( 3.7 \times 10^{-5} )</td>
<td>11.4</td>
<td></td>
<td>72</td>
</tr>
<tr>
<td>Ti</td>
<td>1550</td>
<td>( 7.5 \times 10^{-5} )</td>
<td>50.6</td>
<td>0.01 - 0.02% oxygen present</td>
<td>129</td>
</tr>
<tr>
<td>Zr</td>
<td>1550</td>
<td>( 18.8 \times 10^{-5} )</td>
<td>36.1</td>
<td>- &quot; -</td>
<td>129</td>
</tr>
<tr>
<td>V</td>
<td>1450</td>
<td>( 7.7 \times 10^{-5} )</td>
<td>7.2</td>
<td></td>
<td>128</td>
</tr>
<tr>
<td>Nb</td>
<td>1450</td>
<td>( 5.0 \times 10^{-5} )</td>
<td>7.6</td>
<td></td>
<td>128</td>
</tr>
</tbody>
</table>

### TABLE 11  The self-diffusion of carbon in carbides

<table>
<thead>
<tr>
<th>Carbide</th>
<th>( D, \text{cm}^2/\text{sec} ) (approximate)</th>
<th>Temperature, °C</th>
<th>( Q, \text{kcal/mole} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC</td>
<td>( 10^{-11} )</td>
<td>1450</td>
<td>105</td>
</tr>
<tr>
<td>HfC</td>
<td>( 10^{-13} )</td>
<td>&quot;</td>
<td>130</td>
</tr>
<tr>
<td>VC</td>
<td>( 10^{-10} )</td>
<td>&quot;</td>
<td>67</td>
</tr>
<tr>
<td>NbC</td>
<td>( 10^{-10} )</td>
<td>&quot;</td>
<td>75</td>
</tr>
<tr>
<td>TaC</td>
<td>( 10^{-12} )</td>
<td>&quot;</td>
<td>100</td>
</tr>
<tr>
<td>Mo₂C</td>
<td>( 10^{-8} )</td>
<td>&quot;</td>
<td>60</td>
</tr>
<tr>
<td>WC</td>
<td>( 10^{-17} )</td>
<td>&quot;</td>
<td>90</td>
</tr>
</tbody>
</table>
1.3. **Experimental Considerations**

1.3.1. **The Powder Metallurgy and Sintering of Cemented Carbides**

1.3.1.1. **The Handling of Carbide and Metal Powders**

Most fine powders are liable to atmospheric oxidation or, at least to surface adsorption of oxygen and moisture, at room temperature. In particular, cobalt is known to be quite susceptible to oxidation at room temperature in air\(^{(134)}\). Little is known about the room-temperature oxidation of carbide powders, but Babich et al. measured the atmospheric oxidation of WC-Co compacts and concluded that the weight gain was due only to the oxidation of the cobalt\(^{(135)}\). The weight gain exhibited a logarithmic time dependence, and after 100 minutes corresponded to 0.12 wt% of the cobalt.

1.3.1.2. **The Mixing and Milling of Cemented Carbide Powders**

Commercial cemented carbide powders are prepared by milling together the constituent carbide and metal powders. The milling is said not only to give efficient mixing but also to smear out the metal particles over the harder carbide particle surfaces, and thereby to enhance sintering\(^{(1)}(60)\). At the same time the particle size of the powders is reduced, and the carbide particles become strained\(^{(1)}(60)(136)(137)\). Further improvement in mixing can be achieved by mixing or milling in a fluid\(^{(1)}\).

During milling, contamination of the powders by the milling bodies, the mill walls, and by oxidation, is difficult to avoid. Sometimes the oxidation can lead to decarburisation of the carbide\(^{(1)}(137)\). The extent of oxidation clearly depends on the nature of the powders themselves, as well as on the milling conditions. Both WC\(^{(1)}\) and TiC\(^{(138)}\) are decarburised when milled in water, and TiC is decarburised to a smaller extent when milled in ethyl alcohol or acetone\(^{(138)}\).

1.3.1.3. **The Pressing of Cemented Carbide Powders**

The variables of pressing, such as pressure and the use of pressing lubricants, are adjusted according to the particular alloy, to give fault-free compacts. They seem to have little effect on the efficiency of densification during sintering\(^{(60)}\). Compacting pressures suitable for cemented carbides, range from about 2000 to 10,000 kg/cm\(^2\) (= 12 - 60 tsi)\(^{(1)}(139)\).
1.3.1.4. The Sintering Environment

Cemented carbides are very susceptible to oxidation at elevated temperatures, and sintering environments are chosen to prevent this. Most commonly, sintering is carried out in purified hydrogen or in high vacuum (~10^-4 torr)(1). Even so, oxygen is nearly always present to some extent in the sintering atmosphere, or it may be introduced on the surface of the powders - in particular on the cobalt. During heating, therefore, the following reactions can occur:

\[
2 \text{M}^{6+}\text{C} + \text{O}_2 \rightarrow (\text{M}^{6+}\text{C} - \text{M}^{4+}\text{O}) + \text{CO}_2 \quad (27)
\]

in sintering atmosphere

\[
2 \text{M}^{6+}\text{C} + 2(\text{O}) \rightarrow (\text{M}^{6+}\text{C} - \text{M}^{4+}\text{O}) + \text{CO}_2 \quad (28)
\]

from metal oxides

In some carbides the oxidation results merely in decarburisation without contamination of the carbide with oxygen. Storms has stated that, for the group IV metal carbides, reaction (27) occurs at vacuums worse than 10^-6 torr.(3).

In industrial practice, compacts are usually pre-sintered in a stream of hydrogen, prior to sintering, partly in order to reduce the oxides present on the powders(1). However, this treatment is probably unsuccessful for alloys containing the group IV carbides, because of the high stability of the group IV transition metal oxides (3).

A further problem is that hydrogen itself can decarburise the carbides, by forming hydrocarbons, in certain circumstances. Such decarburisation continues indefinitely in flowing hydrogen.(3) Very recent studies have indicated that the best quality cemented carbides and the best control of carbon content are achieved in high-vacuum furnaces (140)(141).

As well as consideration of the sintering atmosphere, attention has to be paid to the choice of the sintering substrate, because the binder phase - being liquid - is particularly susceptible to reaction with other materials(74)(97). As an example of this, carburisation and the formation of free carbon in the microstructure can sometimes result from embedding compacts in graphite or graphite/alumina powder mixtures, sometimes used as protection from the atmosphere(51).
1.3.2. General Metallography of Cemented Carbides

The basic techniques for the metallographic preparation and examination of commercial cemented carbides are well established\(^{(1)}\). These techniques have been found to be applicable, with only minor modifications, to alloys of experimental compositions\(^{(39)-(40)}\).

The preliminary grinding of sections must be carried out on diamond-impregnated grinding wheels. Polishing can be performed on standard diamond polishing wheels. There are a number of etching techniques which reveal the microstructure. Commonly used etches are, Murikami's reagent (an aqueous solution of 20% KOH and 20% potassium ferricyanide), and solutions of KOH used electrolytically. Heat tinting\(^{(1)}\), thermal etching in vacuum\(^{(89)}\), and ion etching\(^{(142)}\) have also been used successfully.

For most purposes, the microstructure may be observed with optical microscopy, but for accurate quantitative metallography of fine-grained alloys (\(d\) less than about 3 microns), the electron microscopy of replicas is recommended\(^{(37)-(38)}\).

1.3.3. The Quantitative Metallography of Cemented Carbides

1.3.3.1. Quantitative Parameters and their Measurement

The microstructural parameters defined in 1.1.5.1. can also be defined in terms of the measurable parameters of quantitative metallography.

1) The volume fraction of the binder phase.

The volume fraction of the binder phase is given by:

\[
\alpha = \frac{V_1}{V_1 + V_s}
\]

where \(V_1\) and \(V_s\) are the volumes of the binder phase and of the carbide in the alloy, respectively (for the sake of consistency the subscripts 1 and s are used throughout, even for the room-temperature structure). If the microstructure has no orientation dependence, the value of \(\alpha\) is given by an analogous equation involving areas of the phases observed on a random cross-section. The most convenient method of measuring \(\alpha\) is by a process of point counting, in which it is given by
the fraction of random points on a section of the microstructure which fall on the binder phase areas:

\[ \alpha = \frac{P_1}{P_1 + P_s} \]  

(29)

Hilliard and Cahn analysed statistically the various methods of the determination of \( \alpha \) by quantitative metallography and concluded that the most efficient method was the counting of a regular grid of points on the microstructure, such that the grid spacing was of similar dimensions to the size of the areas of the phase being measured \((143)\).

ii) The counting of features.

\( N_A \), the number of a given feature (e.g. particles or cobalt spheres) per unit area of cross-section, can be readily measured on microsections by direct counting. \( N_V \), the number per unit volume, can be derived accurately by determination of \( N_A \) and the size of the features, but only for certain, well-defined shapes \((145)\). If there is a distribution of sizes, the determination of \( N_V \) becomes very arduous.

iii) The carbide grain size.

If a random line is drawn through the microstructure of a cemented carbide, then the mean intercept length of the carbide grains is given by the total length, \( L_s \), intercepting the carbide phase, divided by the number of grains intersected \((145)\). If the line intersects \( N_{ss} \) contiguous carbide grain boundaries, and \( N_{sl} \) carbide/binder interfaces then:

\[ \bar{d} = \frac{L_s}{N_s} = \frac{2L_s}{N_{sl} + 2N_{ss}} \]

The volume fraction of the binder phase can also be expressed in terms of linear intercepts \((145)\):

\[ 1 - \alpha = \frac{L_s}{L_t} \]

where \( L_t \) is the total length of the random intercept line. Therefore:

\[ \bar{d} = \frac{(1 - \alpha)L_t}{N_s} = \frac{2(1 - \alpha)L_t}{N_{sl} + 2N_{ss}} \]  

(30)
Equation (30) implies that the grain size, measured in terms of $\bar{d}$, can be determined by a method involving only counting (i.e. point counting and the counting of grains or grain boundaries).

The mean intercept length can be related to the characteristic dimensions of particles of specific shapes, as will be seen in (v).

iv) The carbide grain size distribution.

The various methods of measuring the true, three-dimensional distribution of grain sizes from a two-dimensional section, have been reviewed by Underwood (45). All the methods are based on the assumption that the particles are spherical. It has been suggested that some of these methods may be applied to equiaxed, non-spherical particles to give a useful approximation to the true distribution (37)(144). It has been shown, however, that cubes (145)(146), and triangular prisms (the WC grain shape), exhibit a wider apparent distribution in two-dimensions than do spheres. For example, a simulated microstructure of uniformly-sized, triangular prisms in a matrix appeared to have a range of prism sizes when analysed with one of the methods based on the assumption of spherical shape (147). Similarly, if a spherical distribution-analysis is performed on the chord-length distribution of a cube (146), the derived distribution of sizes is very much distorted towards low sizes and also exhibits a range of sizes (section 2.2.2.).

Myers has suggested a method for the measurement of the distribution of cubic particles which avoids this problem (148). However, this method cannot be applied to those cemented carbides that have cubic grains, because their shape is distorted by impingement (104).

Exner has derived the theoretical, two-dimensional chord distribution for spherical and cubic particles, which would result from the three-dimensional distributions of the Wagner growth model. Experimental chord distributions can be compared with these and so the transformation of the experimental distributions to three-dimensional distributions is avoided (79)(81). Again, the method fails if the particle shape is distorted.

v) The carbide grain shape.

When a three-dimensional array of randomly-orientated particles, of a specific geometric shape, is cross-sectioned, it will reveal a certain distribution of various two-dimensional shapes (149). Myers was able to predict theoretically the relative proportions of
two-dimensional shapes - expressed in terms of the number of sides - generated by certain regular, uniformly-sized polyhedra when cross-sectioned. For an array of cubes, the following was predicted:

**No. of sides on the shape:** 3 4 5 6

**Frequency of the shape:** 0.28 0.487 0.187 0.016

For cemented carbides, this analysis can only be a guide because of the distortion of the characteristic shape by impingement.

A satisfactory, quantitative means of describing or measuring grain shape is not available. A large number of shape coefficients and parameters exist, but none can define every aspect of shape. It is necessary to choose the parameter that is best suited to the required application. A number of methods of shape measurement involve the comparison of a parameter such as the perimeter length or the surface area per particle, with the same parameter for a sphere of the same size.

The total surface area per unit volume, of any feature, is readily measured by a counting technique. Thus, the area per unit volume of a particular interface is given by:

\[
S = 2 N_{AB}
\]  

(31)

where \( N_{AB} \) is the number of intersections made by the interface on a random intercept line of unit length. To determine the surface area per particle, it is also necessary to determine \( N_y \), which as discussed above in (ii), can only be accomplished for certain shapes. Therefore, this method of shape characterisation is rather limited.

Each shape has a characteristic value of mean linear intercept. For a number of simple shapes, the relationship between \( d \) and the other dimensions of the shape has been derived, for particles of uniform size. Thus,

- for a sphere:
  \[
  d = \frac{lu}{3}
  \]  

(32)

- for a cube:
  \[
  d = \frac{2a}{3}
  \]  

(33)

- for a circular plate:
  \[
  d = 2t
  \]  

(34)

where \( a \) is the cube edge length, and \( t \) is the plate thickness. It is of interest to note that if the effective radius of a cube is used (section 1.2.1.4.1.) the equations for sphere and cube are the same.
vi) The contiguity of the carbide.

It follows from the definition of contiguity that the contiguity of the carbide phase in cemented carbides is given by (35):

\[
G = \frac{2 N_{ss}}{N_{sl} + 2 N_{ss}}
\]

It can therefore be determined by counting the number of the two kinds of interface, intersected by a random line in the microstructure.

vii) The continuity of the carbide phase.

A measure of the continuity is the average number of contacts per particle. To determine this accurately, it is necessary to measure the number of particles and the number of contacts per unit volume. This is straightforward if the particles are uniform spheres and if the areas of contact are uniform, flat discs. For this ideal case:

\[
\bar{N}_C = \frac{2 N_{VSS}}{N_{VP}} = \frac{8}{\pi^2} \left[ \frac{N_{Ass}}{N_{Ap}} \right]^2 \frac{N_{sl} + 2 N_{ss}}{N_{ss}} = \frac{16}{\pi} \left[ \frac{N_{Ass}}{N_{Ap}} \right]^2 \left( \frac{N_{Ass}}{N_{Ap}} \right)
\]

where \( N_{VSS} \) and \( N_{Ass} \) represent the number of contacts between particles per unit volume and per unit area, respectively; similarly, \( N_{VP} \) and \( N_{Ap} \) represent the number of particles. Strictly, equation (36) will not apply for real systems of non-spherical and non-uniform particles, but can probably be used as a relative measure of contact.

viii) The mean free path of the binder phase.

By its definition, the mean free path, \( \bar{l} \), of the binder phase is given by:

\[
\bar{l} = \frac{L_t}{N_l} = \frac{2 L_t}{N_{sl}}
\]

where \( N_l \) is the number of areas of binder phase intersected by a random line of length \( L_t \), passing through the microstructure. By combining equations (30), (35), and (37), equation (25) is obtained (section 1.2.4.), which allows the determination of \( \bar{l} \) from \( \bar{d} \), \( G \), and \( \alpha \).

ix) The dihedral angle.

Isotropic particles, dispersed in a matrix, which have taken up an equilibrium configuration, have theoretically a unique dihedral angle, determined by equation (24). However, in a two-dimensional section,
this angle will be revealed as a distribution of apparent angles. Although the most frequently observed angle in the section is a close approximation to the true dihedral angle \( (\gamma) \), the analysis of Harker and Parker showed that the median value of the distribution is closer to the true angle \( \gamma \). For particles that exhibit anisotropy, the value of \( \phi \) is not given by equation \( (\gamma) \), and, in fact, takes on a range of values which causes a widening of the observed distribution \( (\gamma) \).

1.3.3.2. Errors and Precision of Measurement

The measurements of quantitative metallography are subject both to the statistical errors of sampling, and to errors of experimental technique. The statistical errors can be well defined mathematically, and in general, are minimised by making an adequate number of measurements \( (\gamma) \). The most common sources of error in experimental technique are poor preparation of the microsection and insufficient resolution of the microscope \( (\gamma) \). In practice, it is necessary to choose a field of view with best resolution, consistent with the convenient attainment of adequate sample size. Direct measurement in the microscope is convenient for many purposes, but leads to operator fatigue and the consequent possibility of operator error. For the most accurate work, measurements are usually carried out on enlarged photographs, which also provide a convenient, permanent record for later reference.

Quantitative television microscopes are capable of very rapid measurement, and so statistical sampling errors can be made extremely low. However, such instruments have a somewhat poorer resolution than ordinary microscopes and cannot be used on the very fine microstructures normally encountered in cemented carbides. Furthermore, such instruments are not normally capable of measuring the degree of contact between particles, or of counting contiguous particles separately.

1.3. The Measurement of Interfacial Energies

The multiphase equilibrium method for the determination of surface and interfacial energies has been described in detail by Hondros \( (\gamma) \), and Hodkin et al who used it successfully to determine the surface energies of Nb, Ta, Mo and W, with copper as the liquid metal \( (\gamma) \).
The method can be discussed most easily by reference to Figure 10. Under equilibrium conditions, a groove forms on a solid surface where it is intersected by a grain boundary. The equilibrium geometry of the groove is dictated by the relative values of the surface energy and the grain-boundary energy such that:

\[ \cos \frac{\theta}{2} = \frac{\gamma_{ss}}{2 \gamma_{sv}} \]  

where \( \theta \) is the groove angle, formed by the solid surface at the grain boundary (Figure 10,iii). If \( \gamma_{lv} \) is known, and \( \theta \), \( \phi \), and \( \psi \) are measured, then by combination of equations (2h), (26) and (38), the values of \( \gamma_{sv} \), \( \gamma_{sl} \), and \( \gamma_{ss} \) can be evaluated.

The value of \( \theta \) is determined by the sessile-drop method, by melting a drop of the metal on the polished surface of a polycrystalline specimen of the solid (27)(112). The value of \( \phi \) can be measured on a metallographic section, as described in section 1.3.3.(ix). The value of \( \psi \) can be measured on the polished surface of the polycrystalline solid, after it has been annealed at the relevant temperature, by the use of an optical interference fringe technique (114)(116). The value of \( \gamma_{sv} \) that is obtained will be that for the interface between the solid and the furnace atmosphere. For the method to be strictly correct, the grooving specimen should be annealed in the same atmosphere that the sessile-drop experiment is carried out in.

1.3.5. The Chemical Analysis of Cemented Carbides

1.3.5.1. Overall Analysis

Analysis of the metallic constituents of sintered cemented carbides is normally carried out by crushing a sample, dissolving it in a strong acid mixture, and subsequently using standard methods of analysis of the solution.

The carbon content of the sintered alloys is generally measured by combustion of a crushed sample in a stream of pure oxygen at about 900°C (154). The resulting CO₂ is absorbed in weighing bottles. An estimation of the combined carbon content of a carbide phase can be made 'in situ' by measuring the lattice parameter of the phase (6)(16)(17), although the determination by this means requires some knowledge of the oxygen and nitrogen contents of the carbide.
FIGURE 10  A schematic illustration of the multiphase equilibrium method for determining interfacial energies.

(\(L = \text{liquid; } S = \text{solid; } V = \text{vapour, or vacuum}\))
The best method for the determination of the oxygen and nitrogen contents of carbides is fusion analysis, in which a sample is melted together with platinum. The evolved gases are collected and analysed. Even for this method, the accuracy of the results is somewhat uncertain, particularly in the case of the group IV carbides.

1.3.5.2. Phase Analysis with Electron Probe Micro-analysis

For the purposes of this discussion it will be assumed that the general principles of electron probe micro-analysis (EPMA) are sufficiently well known, to require only the briefest description. The technique is an extremely valuable means of analysis of the distribution of elements within the microstructure of multiphase materials. However, it seems to have rarely been applied to the study of cemented carbides. The reason for this is, probably, that the microstructures of commercial alloys are usually too fine to allow the accurate analysis of individual phases, because, at very best, the lower limit of the size of the area that can be analysed is in the order of one micron. Nevertheless, the technique has been used successfully to reveal the distribution of Mo, Ti and Ni in TiC-Ni-Mo alloys.

To improve the accuracy of the quantitative results obtained by EPMA, it is normally necessary to apply certain corrections to the raw data. The correction procedures have been reviewed recently in detail by Martin and Poole and will not be discussed here.

1.3.6. The Measurement of the Mechanical Properties of Cemented Carbides

Cemented carbides may be classed as brittle materials and consequently, the measurement of their strength is extremely sensitive to the conditions of measurement and the condition of the specimen. Thus it has been found that experimental strength values are very sensitive to the nature of the porosity in the specimen; to the condition of the surface of the specimen; and to the size of the specimen. These are all factors which are associated with the statistical probability of the presence of a critically-sized flaw on the potential fracture surface.

The most commonly measured strength parameter is the transverse rupture strength. The measurement is usually performed on at least 20 specimens of the alloy to be tested, and the strength value is
The determination of the hardness of cemented carbides presents less of a problem than the measurement of strength. The hardness measurement is carried out on the polished surface of a specimen, with the Rockwell A test or the Vickers Pyramid test\(^1\). The Vickers hardness test may also be made use of in an estimation of the toughness of cemented carbides, by observation of the cracks that are generated from the corners of the indentation at heavy loads\(^1\).

Palmqvist developed a method which relates the observed lengths of such cracks to the energy of crack initiation\(^1\). Exner has since pointed out the necessity of eliminating the surfaces stresses that result from specimen preparation, if reliable results are to be obtained by this method\(^1\). Furthermore, he showed that, if the stresses are adequately removed, the total length, \(L_c\), of the cracks generated by an indentation is directly proportional to the indentation load, \(P_h\), and that the plot of \(L_c\) vs. \(P_h\) passes through the origin. Thus the parameter \(P_h / L_c\) becomes a convenient measure of the relative resistance to cracking of the microstructure\(^1\). The Palmqvist technique has the advantage that it can be carried out on single specimens, and that it is not as sensitive to flaws in the specimen as are normal strength measurements.

1.4. Objectives of the Present Investigation in the Context of Chapter 1

The discussions of Chapter 1 have made clear the many factors that can determine the appearance and behaviour of the microstructure of cemented carbides, although the precise role of these remains unclear in many instances.

It is the purpose of the present investigation to achieve a clearer understanding of the effect of these factors, by the thorough and quantitative investigation of the microstructure of a comprehensive range of cemented carbide alloys. The alloys that are studied include alloys of the group IV and V cubic monocarbides, as well as Mo\(_2\)C and WC, with cobalt as binder phase. The physico-chemical properties of these systems are investigated in order to establish more precisely the relationships between these and the important microstructural parameters, such as grain size, grain shape, and the contact between grains, as well as the mechanisms by which they
develop during liquid-phase sintering. Particular attention is paid to the mechanisms of grain growth in these alloys, in view of the apparent lack of agreement and the unresolved problems in much previous work, as revealed in Chapter 1.

The studies are extended to alloys containing mixtures of certain of the carbides, in order to determine the effect of carbide composition on the microstructure. The mixed carbide alloys are chosen to represent solid-solution carbide systems (TaC-NbC; TiC-WC), and systems containing two separate carbide phases (NbC-Vc).

The opportunity is also taken to investigate the relationship between certain mechanical properties of the alloys and their microstructure.
CHAPTER 2

EXPERIMENTAL PROCEDURE

2.1. Preparation of the Alloys

2.1.1. Materials

The investigation was carried out with the highest purity carbide and metal powders that were available commercially. Details of the starting powders are given in Table 12. Most of the carbides were supplied by Hermann C. Starck Berlin, via the London and Scandinavian Metallurgical Company, and were prepared by a technique involving the reaction of the pure transition metal with carbon. They were chosen with a bound-carbon content as close to the theoretical stoichiometric value as possible, consistent with as little free carbon as possible. They were received in the unmilled state.

The TiC powder supplied by the London and Scandinavian Metallurgical Company was subsequently found to have a very wide particle size distribution. A second powder was therefore obtained from the Adamas Carbide Corporation, USA. This had a much narrower particle size distribution, as well as a more satisfactory carbon content.

All the powders were stored in pure, dry argon.

2.1.2 The Preparation of the Alloy Powders

A summary of the compositions of alloys chosen for the investigation are presented in Table 13. The single carbide alloys were chosen to cover all the cubic monocarbides. The alloy of Mo₂C was chosen to observe the effects on the microstructure of changing the crystallographic nature of the carbide, and for the sake of completeness. The alloys of the mixed NbC-TaC, and TiC-WC systems represent mixed carbides of complete, substitutional intersolubility. The alloys of the NbC-VC system represent a system with a miscibility gap, such that at certain temperatures and compositions a VC-rich and a NbC-rich phase co-exist.

The compositions of all the alloys were pre-determined to contain a little over 20 vol% cobalt (except in studies of the effect of cobalt content). Allowing for some loss of cobalt during sintering, this was intended to lead to approximately 20 vol% binder phase in the sintered microstructure. In some alloys, small amounts of graphite
TABLE 12 Details of the as-received carbide and metal powders

<table>
<thead>
<tr>
<th>Carbide or metal (wt%)</th>
<th>Total C wt%</th>
<th>Free C wt%</th>
<th>Stoich. C wt%</th>
<th>Particle size, µm</th>
<th>Main impurities, wt%</th>
<th>Suppliers</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC</td>
<td>19.21</td>
<td>0.14</td>
<td>20.05</td>
<td>3.7</td>
<td>&lt;0.3</td>
<td>Si&lt;0.3; Fe&lt;0.1</td>
</tr>
<tr>
<td>TiC</td>
<td>19.51</td>
<td>0.10</td>
<td></td>
<td>4.1</td>
<td>not given</td>
<td></td>
</tr>
<tr>
<td>ZrC</td>
<td>11.48</td>
<td>0.20</td>
<td>11.64</td>
<td>3.8</td>
<td>0.27</td>
<td>0.07</td>
</tr>
<tr>
<td>HfC</td>
<td>6.31</td>
<td>0.30</td>
<td>6.30</td>
<td>n.d.</td>
<td>0.06</td>
<td>0.11</td>
</tr>
<tr>
<td>VC (1)</td>
<td>18.42</td>
<td>1.20</td>
<td>19.08</td>
<td>n.d.</td>
<td>0.03</td>
<td>0.005</td>
</tr>
<tr>
<td>VC (2)</td>
<td>17.20</td>
<td>0.11</td>
<td></td>
<td>4.5</td>
<td>0.10</td>
<td>0.04</td>
</tr>
<tr>
<td>NbC</td>
<td>11.12</td>
<td>0.02</td>
<td>11.15</td>
<td>7.0</td>
<td>n.d.</td>
<td>Ta 0.08; Fe 0.03</td>
</tr>
<tr>
<td>TaC</td>
<td>6.21</td>
<td>0.11</td>
<td>6.23</td>
<td>2.4</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Mo₂C</td>
<td>5.86</td>
<td>0.02</td>
<td>5.83</td>
<td>3.1</td>
<td>0.06</td>
<td>0.02</td>
</tr>
<tr>
<td>WC</td>
<td>6.10</td>
<td>0.02</td>
<td>6.13</td>
<td>3.2</td>
<td>n.d.</td>
<td>Mo 0.05; Fe 0.03</td>
</tr>
<tr>
<td>NbC-1OTaC</td>
<td>10.38</td>
<td>0.03</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NbC-3OTaC</td>
<td>10.08</td>
<td>0.59</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NbC-75₃₅TaC</td>
<td>7.56</td>
<td>0.14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WC-3OTiC</td>
<td>10.16</td>
<td>0.23</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WC-5OTiC</td>
<td>13.03</td>
<td>0.23</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>graphite</td>
<td>99.999</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cobalt</td>
<td>purity 99.9</td>
<td>1.4</td>
<td></td>
<td></td>
<td>CaO 0.028; Ni 0.025; H₂ loss 0.45</td>
<td>Citricide Ltd.</td>
</tr>
<tr>
<td>niobium</td>
<td>purity 99.9</td>
<td>&lt;10</td>
<td></td>
<td></td>
<td>N 0.01; Fe 0.01; the rest&lt;0.013</td>
<td>Metals Research</td>
</tr>
</tbody>
</table>

* Mean particle size measured with Fisher sub-sieve sizer.
<table>
<thead>
<tr>
<th>Phases expected in the cemented carbide.</th>
<th>The composition of the carbide phases</th>
<th>wt%</th>
<th>mol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC + Co binder</td>
<td>TiC</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HfC + Co binder</td>
<td>HfC</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ZrC + Co binder</td>
<td>ZrC</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>VC + Co binder</td>
<td>VC</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NbC (sub-stoichiometric) + Co binder</td>
<td>NbC (as-received carbide &amp; Co used)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NbC (stoichiometric) + Co binder</td>
<td>NbC (pre-reduced Co used &amp; C added)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TaC + Co binder</td>
<td>TaC</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mo$_2$C + Co binder</td>
<td>Mo$_2$C</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>WC + Co binder</td>
<td>WC</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(Nb,Ta)C + Co binder</td>
<td>NbC - 5 TaC</td>
<td>NbC</td>
<td>NbC - 5 TaC</td>
</tr>
<tr>
<td>(Nb,Ta)C + Co binder</td>
<td>NbC - 18.5 TaC</td>
<td>NbC</td>
<td>NbC - 18.5 TaC</td>
</tr>
<tr>
<td>(Nb,Ta)C + Co binder</td>
<td>NbC - 62 TaC</td>
<td>NbC</td>
<td>NbC - 62 TaC</td>
</tr>
<tr>
<td>(Ti,W)C + Co binder</td>
<td>TiC - 22 WC</td>
<td>TiC</td>
<td>TiC - 22 WC</td>
</tr>
<tr>
<td>(Ti,W)C + Co binder</td>
<td>TiC - 42 WC</td>
<td>TiC</td>
<td>TiC - 42 WC</td>
</tr>
<tr>
<td>(Nb,V)C + Co binder</td>
<td>NbC - 27 VC</td>
<td>NbC</td>
<td>NbC - 27 VC</td>
</tr>
<tr>
<td>(V,Nb)V + trace of (V,Nb)V + Co binder, at 1380°C</td>
<td>NbC - 43 VC</td>
<td>NbC</td>
<td>NbC - 43 VC</td>
</tr>
<tr>
<td>(V,Nb)V + trace of (V,Nb)V + Co binder, at 1380°C</td>
<td>NbC - 61 VC</td>
<td>NbC</td>
<td>NbC - 61 VC</td>
</tr>
<tr>
<td>(V,Nb)V + trace of (V,Nb)V + Co binder, at 1380°C</td>
<td>NbC - 80 VC</td>
<td>NbC</td>
<td>NbC - 80 VC</td>
</tr>
</tbody>
</table>

*The Co content is variable, but in most alloys is about 20 vol%*
were added to compensate for the low carbon contents of the carbide. To the alloy of NbC - 30wt% TaC, metallic niobium was added to compensate for the excess carbon content.

The cobalt was added, either in the as-received condition, or after pre-reduction in pure hydrogen. The pre-reduction was accomplished by passing high-purity, dried hydrogen over the cobalt, heated to 350°C in a pyrex tube, for about two hours. After the treatment, the tube was sealed and subsequently opened in a pure argon atmosphere. Because the reduction process led to caking of the cobalt, it was milled for some hours in a sealed, cobalt-lined rod mill, filled with argon. The alloys prepared with the pre-reduced cobalt were weighed up under argon. These precautions were taken to minimise the introduction of oxygen into the alloys of those carbides which are particularly sensitive to oxidation (section 1.3.1.).

The alloys were weighed into polythene bottles which were then completely filled with a mixing fluid. The mixing fluids were acetone, petroleum ether, or benzene, all of 'Analar' quality. Benzene contains no oxygen as part of its molecule and for this reason it was used in the mixing of TiC, ZrC, and HfC, and certain other alloys, for which exposure to oxidising conditions was to be minimised.

The alloy powders were mixed (not milled), by fastening the bottles to a rotating shaft, for 24 hours. Milling was avoided because this would introduce an extra variable into the process, as well as increasing the likelihood of oxidation. It was subsequently found that milling did not noticeably affect the efficiency of densification of the alloys. After mixing, the powders were kept immersed in the milling fluid until pressed into specimens, immediately before sintering.

A hardened steel die was used to press cylindrical compacts, about 10 mm in diameter and between 5 and 10 mm in height, at a pressure of 4000 kg/cm². During pressing, the powder was usually still moist with mixing fluid, which to some extent acted as a compacting lubricant, as well as affording some protection against the atmosphere. The pressed compacts had green densities of between 63% and 66% of the theoretical density of the alloy. After pressing, the compact was immediately transferred to the sintering furnace, which was then sealed and evacuated.

Exposure of the compact to atmosphere, for up to five minutes
between pressing and evacuation, was unavoidable. The extent to which oxidation could take place was determined by measuring the weight gain of freshly reduced cobalt powder (see section 1.3.1.1.). This was found to be about 0.02 wt% in the first 5 minutes of exposure. Since the alloy compacts contained about 14 to 35 wt% of cobalt, the maximum expected weight gain of an alloy by oxidation would be a corresponding fraction of 0.02 wt%.

2.1.3. Sintering

2.1.3.1. The Sintering Furnace

Sintering was carried out in a modified, Edwards vacuum furnace. The furnace chamber is shown schematically, in cross-section, in Figure 11.

The furnace element and radiation shields were of molybdenum and, held vertically, they surrounded a cylindrical alumina crucible, in which the specimens could be placed on a pedestal. The furnace was powered by a transformer supply of 90 amps at 25 volts, and was capable of attaining a temperature of at least 1600°C.

The temperature in the hot zone was measurable to ± 5°C with a Pt-6%Rh / Pt-30%Rh thermocouple, which almost touched the specimen, and could be controlled to within ± 1°C of a pre-set temperature by use of a Eurotherm, thyristor, temperature controller. The variation in temperature over the dimensions of the specimen was negligible. The thermocouple was frequently calibrated against a fresh thermocouple to check for drift due to contamination, and was replaced when necessary.

With a standard diffusion pump and rotary pump arrangement, a vacuum of between $5 \times 10^{-5}$ and $5 \times 10^{-5}$ was attainable in the furnace.

2.1.3.2. Sintering Procedure

i) The standard procedure.

Specimens were sintered on a substrate of small chips of an alloy of the same carbide as the specimen, or occasionally on a substrate of graphite. The substrate was placed on an alumina pedestal.

Heating was begun after the furnace had been evacuated to $5 \times 10^{-5}$ torr. The specimens were heated from room temperature to a temperature ($\sim 1250 - 1300°C$), somewhat below the eutectic melting
FIGURE 11  Schematic diagram of the sintering furnace
(not exactly to scale)

a) Specimen
b) Radiation shield for thermocouple junctions
c) Thermocouple lead-through
d) Radiation shields
point of the alloy concerned, in about 3 hours. The duration of heating was approximately the same for all alloys, except when the effect of presintering time was investigated. Having reached the above-mentioned temperature, however, subsequent heating to the sintering temperature was carried out as rapidly as possible, in order to minimise the extent of the liquid-phase sintering processes which occurred before the nominal start of sintering. This rapid heating stage was accomplished in 1 to 2 minutes, depending on the temperature to be reached.

Sintering was timed from the instant that the sintering temperature was reached. At the end of sintering, the power was switched off and the specimen allowed to furnace-cool. The time taken to cool from the sintering temperature to about 1300°C (well below the freezing temperature; see Table 8) was between 45 and 90 seconds, again, depending on the sintering temperature. The vacuum during sintering was always between $5 \times 10^{-6}$ and $5 \times 10^{-5}$ torr.

ii) Special sintering cycles.

a) The mixed carbide alloys of NbC with VC were made up from the separate carbide powders. It was found that the alloys of this system that were designed to have two carbide phases had very inhomogeneous microstructures, when sintered by the standard procedure. These alloys were therefore first heated to 1550°C, held there for five minutes, and then cooled rapidly to the required sintering temperature.

b) In order to sinter the VC-Co alloy at 1300°C, at which temperature the binder is solid, the specimens were first heated to 1380°C, held there for five minutes to allow complete densification, and then cooled rapidly to 1300°C for sintering.

2.1.4. The Analysis of Sintered Specimens

To assess the adequacy of the alloy preparation and sintering techniques, a number of sintered alloys were selected for wet chemical analysis by the techniques described in section 1.3.5.1. The analyses were carried out by the B.S.A. Group Research Centre, Birmingham. The results are presented, in terms of the carbon content of the carbide, in Table 14. It is clear from these, that the preparation techniques did not lead to a significant reduction in carbon content and may be considered satisfactory. In general, the C:M\textsuperscript{w} ratios are just below those which would produce free carbon.
TABLE 14  The carbon contents of the carbide in selected specimens

<table>
<thead>
<tr>
<th>Carbide</th>
<th>Sintering Time (min)</th>
<th>Temp (°C)</th>
<th>Carbon, wt% Before*</th>
<th>Carbon, wt% After sintering</th>
<th>Carbon:metal ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>VC</td>
<td>120</td>
<td>1450</td>
<td>17.4</td>
<td>17.5 ± 0.2</td>
<td>0.91</td>
</tr>
<tr>
<td>NbC(as-recc.)</td>
<td>120</td>
<td>1450</td>
<td>11.12</td>
<td>11.15 ± 0.2</td>
<td>0.97</td>
</tr>
<tr>
<td>NbC</td>
<td>0</td>
<td>1450</td>
<td>11.40</td>
<td>11.27 ± 0.1</td>
<td>0.98</td>
</tr>
<tr>
<td>NbC</td>
<td>120</td>
<td>1450</td>
<td>11.40</td>
<td>11.26 ± 0.1</td>
<td>0.98</td>
</tr>
<tr>
<td>NbC</td>
<td>120</td>
<td>1550</td>
<td>11.40</td>
<td>11.44 ± 0.1</td>
<td>1.00</td>
</tr>
<tr>
<td>TaC</td>
<td>120</td>
<td>1450</td>
<td>6.21</td>
<td>6.28 ± 0.1</td>
<td>1.00</td>
</tr>
<tr>
<td>TiC</td>
<td>120</td>
<td>1450</td>
<td>19.51</td>
<td>19.30 ± 0.1</td>
<td>0.95</td>
</tr>
</tbody>
</table>

*Suppliers analysis + added free C, if any.

Attempts to determine the oxygen and nitrogen contents of the alloys were not entirely successful because the specimens did not dissolve completely in the platinum bath, even at temperatures of about 2200°C. The gases that were evolved represented contents in the order of 1 to 10 ppm. In view of the satisfactory carbon contents it is probable that the gas contents were satisfactorily low.

2.2. Metallography

2.2.1. Preparation of the Metallographic Section

The sintered specimens were sectioned at least 1 mm below their surface by grinding, first on a 100 mesh, and then on a 300 mesh diamond-impregnated wheel, with water as coolant. The resulting finish was suitable for polishing on standard diamond polishing wheels, with 7 micron and then 1 micron diamond paste on hard cloth or the back of photographic paper.

The most suitable etch for the majority of the alloys was found to be a freshly-prepared mixture of the aqueous solutions of 20% potassium hydroxide and 20% potassium ferricyanide. The etch was used at temperatures between 20°C and the temperature of boiling of the etch, depending on the carbide in the alloy. In certain cases, other etches were used, depending on the features to be revealed. These will be mentioned in the text as they arise.
It was found that HfC-Co alloys were not etched suitably by any conventional, chemical etches. The microstructure was revealed most satisfactorily for the purposes of quantitative metallography by heating in vacuum for about 30 minutes at 1000°C.

2.2.2. Quantitative Metallography

All quantitative measurements were made on photographs of the microstructures. These were taken at magnifications between 200 X and 1600 X on photographic plates, using an optical microscope, and were subsequently enlarged to between 500 X and 1000 X. The magnification was chosen to suit the coarseness of the microstructure.

i) The measurement of volume fraction.

The volume fraction of the binder phase was measured on each photograph with a grid of 2000 points, such that the grid spacing was similar to the mean free path length of the binder phase (see section 1.3.3.1.). The main source of uncertainty in the measurement was that the carbide/cobalt interface had a finite thickness due to etching. For the purposes of measurement, it was assumed that the interface was at the centre of the etched boundary. For most specimens, counting was carried out on three photographs. The theoretical standard deviation in the mean value of \( \alpha \), due to the statistical sampling error, was in this case \( \pm 0.006 \) for a value of \( \alpha \) of 0.2\(^{143}\).

In fact, the measured standard deviation was slightly greater than this, partly because of real variations in \( \alpha \) from place to place in the specimen (i.e. from photograph to photograph), and partly because of the etching uncertainty mentioned above.

The porosity of the sintered specimens was determined by measurement of the volume fraction of pores with a 'Quantimet', quantitative television microscope. It was also estimated qualitatively by the ASTM-standard method \(^{50}\), mentioned in section 1.1.5.2.

ii) The measurement of contiguity and the mean intercept length of the carbide.

The values of the contiguity and the mean intercept length of the carbide were determined by counting the number of carbide/cobalt interfaces \( N_{sl} \), and the number of carbide grain boundaries \( N_{ss} \), intersected by lines super-imposed on the photographs, and by then applying equations (30) and (35). The total length, \( L_L \), of the
intersecting lines was between 1000 and 8000 microns per photograph, depending on the magnification. This resulted in a count of between 500 and 1000 grains per specimen.

Since \( d \) was determined by counting boundaries rather than by direct linear measurement, the error of measurement was small. The main errors were those introduced by errors in \( \alpha \), and errors of sampling. The main source of error in the value of \( G \) arose from the uncertainty of where very thin layers of binder phase are present between two grains. Increasing the magnification and resolution of the areas examined would reduce this uncertainty, but would also reduce the number of interfaces that could be conveniently counted.

iii) The measurement of grain shape

In the majority of alloys, the shape of the carbide grains was found to be either, well-defined cubic, rounded cubic, or completely rounded. For this reason it was considered that a convenient means of estimating shape was to measure the ratio of the surface area of flat carbide/binder interfaces to the total carbide/binder interfacial area. By analogy with equation (31)* this ratio is given by:

\[
F_A = \frac{S_{\text{flat interfaces}}}{S_{\text{total interfaces}}} = \frac{2 N_{\text{flat interfaces}}}{2 N_{\text{total interfaces}}}
\]

which is readily measured by the counting of intersections on a random test line. This shape factor has the advantage that it requires no prior assumption about the shape (see section 1.3.3.1.v) and is not affected by particle contact. Further implications of the parameter will be discussed in Chapter 5.

A further possible technique for studying grain shape is the use of scanning electron microscopy, which enables individual grains to be examined three-dimensionally. Specimens exhibiting characteristic grain shapes were suspended in a boiling, 20% solution of HCl for some hours, with the result that the cobalt matrix was leached out, leaving the carbide unaffected. Because of its complete continuity the carbide retained its spatial configuration and the specimen stayed whole. It could therefore be conveniently examined in a Cambridge Stereoscan instrument.

iv) The counting of cobalt spheres, grains, and inter-particle contact.

The numbers, \( N_A \), of cobalt spheres, carbide grains and contacts
between grains, per unit area were measured directly from the micro-
graphs of selected specimens. An approximate value for the number of 
contacts per grain was calculated using equation (36).

v) The carbide grain size distribution.

Before attempting to measure the three-dimensional, carbide grain 
size distributions by use of analyses based on the assumption of 
spherical particle shape, it was decided to test the effect of 
development from sphericity on the accuracy of the derived distribution. 
About 400 small steel cubes of edge-length 3.15 mm were dispersed in 
a molten alloy of tin and lead, the composition of which was chosen 
to have a density similar to that of steel in order to avoid segreg-
ation effects. After solidification, the specimen was sectioned in 
a number of random directions and the chord-length distribution of 
the revealed cube sections was determined using a 'Quantimet' quanti-
tative television microscope. A total of about 6000 intercepts was 
measured. A distribution, very similar to that derived theoretically 
by Itoh, was obtained. From this distribution was derived the 
three-dimensional distribution of equivalent diameters, using an 
analysis for spherical particles. The derived distribution errone-
ously predicted a range of particle sizes, and a maximum frequency 
at about 0.1 mm.

It was clear from this that, for the particle shapes observed in 
the alloys of this investigation, such an analysis was insufficient-
ly accurate to justify the considerable effort involved in its 
application. Instead, the more readily measured ratio of the size of 
the largest particle to the mean particle size, $d_m / \bar{d}$, was determined 
by finding the largest particle section in the observed microsection. 
For particles with a cubic shape, the distance between the closest 
parallel edges of a particle section, is a close approximation to the 
edge length, $a$ (116). Using equation (33) it was therefore possible to 
determine $d_m / \bar{d}$ quite accurately. The assumption that the largest section 
found corresponds to the largest section in the whole specimen is 
of course, not strictly justified, and the values of $d_m / \bar{d}$ were 
probably somewhat too low. For particles of near-spherical or irreg-
ular shape, it was assumed that the particles were spheres and $d_m$ was 
taken as two thirds of the diameter of the largest particle section 
(equation 32); and the diameter was taken as the average of the
maximum and minimum linear dimensions. Because the particles were not true spheres, the values of \(d_m\) may have been slightly too large.

2.3. The Measurement of Interfacial Energies

The multiphase equilibrium method, described in section 1.3.4, was used to determine the interfacial energies in certain carbide systems.

2.3.1. The Sessile-drop Experiment

Values of the angle of contact of pure cobalt on carbides have already been determined (112)(113) (Table 8). However, the measurements were repeated on a number of carbides in the sintering furnace of this investigation, in order to obtain values in exactly the same conditions as those of sintering and thermal grooving.

A disc of the polycrystalline carbide, prepared by hot-pressing with the equipment and techniques used by Ramqvist (160), was ground and polished to a surface finish given by 1 micron diamond polish. It was then cleaned ultrasonically in CCl\(_4\). A small specimen of high purity cobalt (Johnson-Matthey, 'Specpure'), cleaned in dilute hydrochloric acid and CCl\(_4\), was placed on the polished surface of the carbide, and the combination was stood on an alumina pedestal in the sintering furnace. Under similar conditions to those of sintering, the system was heated to the temperature of wetting and held there for ten minutes. The value of \(\theta\) was estimated by measurement of the diameter and height of the cooled drop, it being assumed that the drop was a spherical cap (112).

2.3.2. Grain Boundary Grooving

A disc of polycrystalline NbC, prepared and polished in the same manner as for the sessile-drop experiment, was heated in the sintering furnace for ten hours at 1500°C.

The resulting grain-boundary grooves were studied with a Nomarski-type interferometer, on a Reichert microscope, at a magnification of 1400 X and with mercury vapour illumination \(\lambda = 5461 \text{ A}\). Suitable interference patterns were photographed and subsequently enlarged to 4000 X. The surface of the annealed carbide exhibited a considerable amount of faceting, which distorted most of the groove profiles and it was not possible to find more than 13 undistorted grooves.
A number of attempts to carry out the similar thermal grooving of TiC, failed because of the contamination of the surface.

The method of determining the value of $i'p$ from the interference pattern has been described by Hodkin et al. (116). The width of the groove, $b$, is measured at one fringe spacing, whence:

$$\tan \frac{i'}{2} = \frac{b}{(M \times 1.1 \lambda)}$$

where $M$ is the magnification of the photograph. The factor of 1.1 is a correction factor, necessary when high-aperture objective lenses are used (116).

2.3.3. The Measurement of Dihedral Angle

Values of dihedral angles, $\phi$, were determined from the micrographs used for the other quantitative metallographic measurements. At least 100 apparent dihedral angles were measured for a given specimen, and the median angle of these was determined. For the purposes of the multiphase equilibrium determination of interfacial energies in the NbC-Co system, measurement was made on an alloy sintered at 1550°C, since at lower temperatures the carbide grains exhibited anisotropy of shape, sufficient to make the meaning of the measured $\phi$ uncertain (see section 1.3.3.1.ix).

2.4. The Measurement of Solubility

During the sessile-drop experiment, the pure liquid metal takes into solution material from the solid substrate. The opportunity was therefore taken to analyse the cobalt drop after the wetting of the carbides, in order to obtain values for the solubilities of those carbides in liquid cobalt, at the temperature of the wetting experiment. To do this, it is necessary to assume that the cobalt takes up the equilibrium quantity of carbide during wetting.

The drop was sectioned vertically, polished, and then etched in a dilute solution of ferric nitrate in nital. The etch revealed a very fine eutectic-type microstructure, together with some primary dendrites, in all cases (Figure 12). Analysis of the drop composition was attempted in two ways:

1) Electron probe micro-analysis.

The drop microsection was examined by electron probe micro-analysis
FIGURE 12  The microstructure of cobalt which has been in contact with NbC at 1550°C and then furnace cooled.

800 X
using a Cambridge 'Geoscan'. It was found that the eutectic structure was too fine to allow sufficient resolution of the two phases for accurate individual analysis. Instead, X-ray counts were taken from a large scanned area and treated as if they were derived from a normal solid solution. The count rate from the transition metal of the carbide was compared to that from a standard of the pure carbide. The usual corrections were made for absorption, fluorescence, and atomic number effects (see section 2.5.) when the transition metal content of the drop was evaluated.

To treat the microstructure as a solid solution in this way is not strictly valid. The separate phases exhibit different characteristics with respect to X-ray absorption, atomic number effect, and fluorescence, compared to those of the hypothetical solid solution of the same composition. On the other hand, because the time spent by the beam on a given phase is proportional to its volume fraction there will be an over-estimation of the less dense phase. For most systems, these two effects will be opposed and to some extent cancel out.

ii) Quantitative Metallography.

The relative proportions of the two phases in the eutectic were determined by point counting on enlarged micrographs. The composition was then calculated by assuming that the metallic phase contained no dissolved carbide, and that the carbide phase was the monocarbide, MnC. Since the cobalt probably retained a little carbide in solution (see Table 9), the values obtained by this method are probably somewhat too low.

2.5. The Investigation of Microstructures with EPMA.

A Cambridge 'Geoscan' electron probe micro-analyser was used to study the distribution of elements in the alloys which contained mixed carbides, and also the special case of the Mo$_2$C-Co alloy. The examinations were carried out on normally prepared, unetched specimens. In the majority of cases, the individual carbide grains were large enough to make accurate point analysis possible. Analysis of the binder phase, which is distributed much more finely, was less reliable, particularly as it was not possible to determine whether or not there were carbide grains just below the spot being analysed.
X-ray counts of the relevant elements were taken from suitable points in the microstructures and compared with counts from a standard, which was usually a carbide of known composition. The raw counts were corrected for the dead time of the X-ray counting instrument. The specimen-standard count ratio was then corrected for: X-ray absorption, using the expression derived by Philibert; for atomic number effect by the method derived by Thomas; and for fluorescence by the method derived by Reed. The overall correction factors varied between 0.93 and 1.26 depending on the system and element being analysed.

2.6. The Measurement of Mechanical Properties

2.6.1. Microhardness

An Akashi microhardness tester with a Vickers pyramid diamond indenter was used to measure the microhardness of individual carbide grains in those alloys with sufficiently coarse grains. Using a load of 100 gm, the indentation diagonal was usually between about 8 and 12 microns, depending on the carbide hardness (2900 to 1290 kg/mm²). If it is assumed that there was an uncertainty of about 0.5 microns in the measurement of the diagonal, then there is an uncertainty of 5 - 10% in the hardness values in this range. For most specimens indentations were made on at least ten different grains.

2.6.2. Macrohardness

A conventional Vickers hardness machine was used to measure the macrohardness of the sintered alloys, at loads between 20 and 100 kg. It was found that for the alloys with very coarse microstructures (VC-Co and to some extent NbC-Co alloys), the indentation was heavily distorted and lost its well-defined square shape. In these cases the measurement of hardness was very uncertain.

2.6.3. Resistance to Crack Formation

Before the hardness tests were carried out, the specimens were polished in accordance with the recommendations of Exner, to remove surface stresses due to grinding. The total length of the cracks, $L_c$, that formed from the corners of the indentations, was measured with the cross-wire optical system of the microhardness.
tester. In some alloys, particularly WC-Co, more than one crack was
Generated from each corner. In such cases, the longest crack was
measured.

In general, it was found that a plot of \( L_c \) vs. the indentation
load \( P_h \), was linear and passed through or close to the origin, which
indicated that surface stresses were, in fact, removed \(^{(159)} \). For this
reason, the parameter, \( W = \frac{P_h}{L_c} \), was used as a measure of the
resistance to cracking, as suggested by Exner \(^{(159)} \).

In the coarser microstructures, the \( L_c vs. P_h \) plot passed through
positive values of \( L_c \) at zero load and this could be attributed to
the fact that at low loads the crack length was determined by the size
of the carbide grain at the corner of the indentation, rather than the
magnitude of the load. For this reason, the value of \( \frac{P_h}{L_c} \) at high
values of \( P_h \) was taken as the most reliable value for the microstruc-
ture as a whole.

A study was also made of the path taken by the cracks, i.e. the
extent to which they passed through the carbide, the binder phase, or
along interfaces.
CHAPTER 3

PRELIMINARY INVESTIGATIONS OF THE ALLOYS

Introduction

The results of the microstructural studies of the many alloys investigated, and the implications of these results, are discussed in detail in later Chapters. In the present Chapter, an overall and preliminary survey of the sintering behaviour and general microstructural properties of all the alloys is given, for the sake of clarity in subsequent Chapters. In addition, the results of the physico-chemical measurements which were made on a number of systems, and the results of the EPMA studies of the microstructures will be presented, since they are of general relevance to subsequent Chapters. A summary of the principle microstructural features of the main alloys investigated, are presented in Table 15.

3.1. General Sintering Behaviour

3.1.1. Densification and Porosity

Because of the rapidity of the processes of liquid-phase densification, it was not possible to make quantitative studies of the sintering rates. The following qualitative observations were made.

The alloys of VC, NbC, TaC, Mo2C, and WC, sintered very rapidly to almost theoretical density. Porosity was almost completely removed within 5 minutes of the sintering temperature being reached, and for VC, NbC, and Mo2C, most of the porosity was removed during heating from the eutectic temperature up to the sintering temperature. These observations are illustrated by the micrographs, Figures 14, 15, 16, 17, 19, and 20. After longer sintering times, the Mo2C alloy developed large bubbles, while the bulk of its microstructure remained pore-free. The best final densities were obtained in the NbC-VC, mixed carbide alloys.

The alloys of the carbides of the group IV transition metals did not sinter so readily. The alloys of TiC quickly sintered to a density of about 95% theoretical, and thereafter approached theoretical density very slowly, reaching 99% after about 8 hours at 1450°C, or 2 hours at 1550°C. The HfC alloy sintered poorly and did not attain densities
greater than about 90% theoretical. The ZrC alloy did not sinter at all, regardless of the sintering time and temperature, or the substrate used. The cobalt sweated from the compact, which indicated that the carbide remained completely unwetted.

These observations are qualitatively consistent with the wettabilities of the systems (i.e. the values of $\gamma_{lv} \cos \theta$, Table 8). With the notable exceptions of the WC-Co and NbC-Vc-Co alloys, there is also a correlation between the densification and the rates of material transport in the systems (the relative values of the rates of transport can be judged approximately from the values of $\alpha$, in Table 15; see also Chapter 4). This is to be expected if solution/precipitation mechanisms of densification, similar to that suggested by Kingery, occur (section 1.1.1.). The very efficient densification of the WC-Co and NbC-Vc-Co alloys, in which the material transport is low, may be attributed to a predominance of the re-arrangement process. In this respect, it is of interest that these alloys contain carbides with relatively high solubilities (Table 21).

The failure of the ZrC-Co alloy to sinter, probably cannot be attributed solely to these effects, since ZrC is wet to a certain extent by liquid cobalt. It is possible that the carbide powder was contaminated with oxygen. A thin layer of oxide on the powder surface would be sufficient to prevent wetting.

In conclusion, it may be stated that densification during liquid-phase sintering is favoured by good wetting (i.e. a high value of $\gamma_{lv} \cos \theta$), and a high rate of material transport, although because of the predominance of the re-arrangement process in certain alloys, the latter condition does not appear to be always essential.

3.1.2. The Presence of Free Carbon and Other Phases

The majority of alloys contained no phases other than the cobalt binder and the intended carbide phases.

However, traces of free carbon were observed in the NbC-Co alloy in which the carbon content had been made up to the stoichiometric value by additions of graphite and by the use of pre-reduced cobalt. The free carbon represented not more than a fraction of a volume percent, but was concentrated at the carbide/cobalt interface and so may have affected the development of the microstructure. However, it
can be assumed that at least some of it precipitated during cooling and consequently, that the amount present during sintering was less than that observed. The presence of free carbon in this alloy illustrates the fact, already mentioned in section 1.1.3., that it is not possible to achieve full stoichiometry in NbC.

For a similar reason, a few specimens of the VC-Co alloys also contained traces of free carbon. In these specimens, however, the free carbon was in the form of precipitated flakes within the binder phase, and did not affect the development of the microstructure during sintering.

There was no evidence of carbon-deficiency, lower carbides in the alloys of the cubic monocarbides, as was anticipated in section 1.1.5. In the Mo₂C-Co alloy, however, a second phase was observed between the grains of Mo₂C, and can be seen in Figure 13. This alloy was investigated by EPMA, and its constitution is discussed in section 3.3.iii).

3.1.3. Precipitation of Carbide during Cooling

As discussed in section 1.2.1.1., it is generally assumed that, during cooling after liquid-phase sintering, the dissolved carbide reprecipitates onto the surface of existing particles. However, in the present investigation, very fine precipitate particles were observed in the binder phases of NbC-Co alloys sintered at 1500°C and 1550°C, and of VC-Co alloys at all sintering temperatures (see Figure 15). Similarly, the binder phase in the Mo₂C-Co alloy was in the form of a very fine eutectic structure (Figure 13). These observations suggest that in cases of high super-saturation and/or large volume fractions of liquid phase, it is kinetically unfavourable for all the carbide to precipitate onto existing grains. For the purposes of quantitative metallographic measurements, such precipitates were counted as part of the binder phase, since during sintering they are part of the liquid.

Two of the NbC-VC-Co alloys also had a fine precipitate within the binder phase. However, the NbC-VC is unusual in having two separate carbide phases, in certain conditions, and these alloys will be discussed in later sections.
TABLE 15 (a) Some microstructural properties of the investigated alloys - single carbides  
(Sintering time: 120 minutes; temperature: 1450°C; or as stated)

<table>
<thead>
<tr>
<th>Alloy (20 vol% Co)</th>
<th>Grain size $d$, microns</th>
<th>$dm/d$</th>
<th>Number of cobalt spheres/mm²</th>
<th>Contiguity $G (\alpha = 0.2)$</th>
<th>Grain shape</th>
<th>Porosity Vol%</th>
<th>ASTM</th>
<th>Extra phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC (L &amp; S)</td>
<td>5.6</td>
<td>3.7</td>
<td>n.d.</td>
<td>0.33</td>
<td>irregular</td>
<td>n.d.</td>
<td>n.d.</td>
<td>none</td>
</tr>
<tr>
<td>TiC (Adamas)</td>
<td>5.5</td>
<td>2.5</td>
<td>150</td>
<td>0.25</td>
<td>cubic, v.rounded</td>
<td>3.96</td>
<td>A1, B3</td>
<td>none</td>
</tr>
<tr>
<td>ZrC</td>
<td>-</td>
<td>-</td>
<td>the compacts did not sinter</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HfC (1500°C)</td>
<td>3.3</td>
<td>2.4</td>
<td>n.d.</td>
<td>0.31</td>
<td>cubic, v.rounded</td>
<td>25.4</td>
<td>B5-B6</td>
<td>none</td>
</tr>
<tr>
<td>VC0,91</td>
<td>35.9</td>
<td>1.8</td>
<td>10</td>
<td>0.10</td>
<td>near spherical</td>
<td>0.1</td>
<td>&lt;A1</td>
<td>0.2 vol% C</td>
</tr>
<tr>
<td>NbC0,97</td>
<td>21.1</td>
<td>2.4</td>
<td>50</td>
<td>0.27</td>
<td>cubic, rounded</td>
<td>0.13</td>
<td>&lt;A1</td>
<td>none</td>
</tr>
<tr>
<td>NbC0,98</td>
<td>18.8</td>
<td>2.2</td>
<td>100</td>
<td>0.31</td>
<td>cubic, slightly rounded</td>
<td>0.2</td>
<td>&lt;A1</td>
<td>0.3 vol% C</td>
</tr>
<tr>
<td>TaC</td>
<td>7.9</td>
<td>2.4</td>
<td>250</td>
<td>0.38</td>
<td>cubic, angular</td>
<td>0.09</td>
<td>A1</td>
<td>none</td>
</tr>
<tr>
<td>Mo2C (1380°C)</td>
<td>29.1</td>
<td>1.6</td>
<td>0</td>
<td>0.2</td>
<td>near spherical</td>
<td>-</td>
<td>&lt;A1</td>
<td>η-phase</td>
</tr>
</tbody>
</table>
### TABLE 15 (b) Some microstructural properties of the investigated alloys - mixed carbides

(Sintering time 120 minutes; temperature 1150°C; or as stated)

<table>
<thead>
<tr>
<th>Alloy composition (20 vol% Co)</th>
<th>Grain size $\bar{a}$, microns</th>
<th>$d_m/\bar{a}$</th>
<th>Number of cobalt spheres/mm$^2$</th>
<th>Contiguity $G(\alpha = 0.2)$</th>
<th>Grain shape</th>
<th>Porosity Vol%</th>
<th>ASTM</th>
<th>Extra phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>NbC - 5 TaC</td>
<td>11.3</td>
<td>-</td>
<td>100</td>
<td>0.35</td>
<td>cubic, rounded</td>
<td>0.22 $&lt; \Delta 1 &lt; \Delta B$</td>
<td>none</td>
<td></td>
</tr>
<tr>
<td>NbC - 16.5 TaC</td>
<td>9.2</td>
<td>-</td>
<td>100</td>
<td>0.38</td>
<td>cubic, slightly rounded</td>
<td>2.33 B2</td>
<td>none</td>
<td></td>
</tr>
<tr>
<td>NbC - 62 TaC</td>
<td>9.0</td>
<td>-</td>
<td>150</td>
<td>0.40</td>
<td>cubic, angular</td>
<td>0.08 $&lt; \Delta 1 &lt; \Delta B$</td>
<td>none</td>
<td></td>
</tr>
<tr>
<td>NbC - 27 VC (t = 180 min)</td>
<td>6.3</td>
<td>-</td>
<td>0</td>
<td>0.39</td>
<td>ill-defined, angular</td>
<td>0.24 $&lt; \Delta 1 &lt; \Delta B$</td>
<td>none</td>
<td></td>
</tr>
<tr>
<td>NbC - 43 VC (t = 180 min)</td>
<td>3.8</td>
<td>-</td>
<td>0</td>
<td>0.45</td>
<td>irregular, rounded &amp; near spherical</td>
<td>0.01 $&lt; \Delta 1$</td>
<td>none</td>
<td></td>
</tr>
<tr>
<td>NbC - 61 VC (t = 180 min)</td>
<td>~1.0</td>
<td>-</td>
<td>n.d.</td>
<td>n.d.</td>
<td>irregular, rounded</td>
<td>0.01 $&lt; \Delta 1$</td>
<td>none</td>
<td></td>
</tr>
<tr>
<td>NbC - 80 VC (t = 180 min)</td>
<td>12.0</td>
<td>-</td>
<td>0</td>
<td>0.40</td>
<td>near spherical</td>
<td>0.01 $&lt; \Delta 1$</td>
<td>none</td>
<td></td>
</tr>
<tr>
<td>TiC - 22 WC</td>
<td>6.6</td>
<td>3.5</td>
<td>130</td>
<td>0.40</td>
<td>cubic, slightly rounded</td>
<td>0.35 $&lt; \Delta 1 &lt; \Delta B$</td>
<td>\text{0.05% C}</td>
<td></td>
</tr>
<tr>
<td>TiC - 42 WC</td>
<td>4.0</td>
<td>3.5</td>
<td>n.d.</td>
<td>0.43</td>
<td>irregular, rounded</td>
<td>0.84 $&lt; \Delta 1 &lt; \Delta B$</td>
<td>\text{0.1% C}</td>
<td></td>
</tr>
</tbody>
</table>
FIGURE 13
The microstructure of the alloy
Mo$_2$C - 20 vol% Co;
sintered at
1380°C for 120 minutes.
(Note extra, white phase within the binder phase)
400 X

FIGURE 14
The microstructure of the alloy
VC - 20 vol% Co;
sintered at
1380°C for 0 minutes
400 X

FIGURE 15
The microstructure of the alloy
VC - 20 vol% Co;
sintered at
1380°C for 120 minutes
400 X
FIGURE 16
The microstructure of the alloy
NbC - 20 vol% Co;
sintered at
1450°C for 0 minutes.
800 X

FIGURE 17
The microstructure of the alloy
NbC_{0.97} - 20 vol% Co;
sintered at
1450°C for 100 minutes.
(ion etched)
400 X

FIGURE 18
SEM picture of the alloy
NbC_{0.97} - 20 vol% Co;
sintered at
1500°C for 120 minutes.
(Cobalt leached out in boiling 20% HCl soln.)
500 X
FIGURE 19
The microstructure of the alloy TaC - 20 vol% Co; sintered at 1450°C for 0 minutes.

800 X

FIGURE 20
The microstructure of the alloy TaC - 20 vol% Co; sintered at 1450°C for 120 minutes.

800 X

FIGURE 21
SEM picture of the alloy TaC - 30 vol% Co; sintered at 1450°C for 48 minutes. (Cobalt leached out in boiling 20% HCl soln.)

1000 X
FIGURE 22
The microstructure of the alloy (NbC-62mol% TaC)-20vol% Co, sintered at 1450°C for 120 minutes.

FIGURE 23
The microstructure of the alloy (NbC-5mol% TaC)-20vol% Co, sintered at 1450°C for 120 minutes.
FIGURE 24
The microstructure of the alloy
(NbC-27mol%VC)-20vol% Co; sintered at 1380°C for 170 minutes. 800 X

FIGURE 25
The microstructure of the alloy
(NbC-43mol%VC)-20vol% Co; sintered at 1380°C for 180 minutes. 1600 X (oil immersion)

FIGURE 26
The microstructure of the alloy
(NbC-61mol%VC)-20vol% Co; sintered at 1450°C for 180 minutes. 1600 X (oil immersion)

FIGURE 27
The microstructure of the alloy
(NbC-80mol%VC)-20vol% Co; sintered at 1380°C for 170 minutes. 800 X
FIGURE 28
The microstructure of the alloy
TiC - 20 vol% Co;
sintered at 1450°C for 120 minutes.
800 X

FIGURE 29
The microstructure of the alloy
(TiC-22mol%WC)-20 vol% Co;
sintered at 1450°C for 120 minutes.
800 X

FIGURE 30
The microstructure of the alloy
(TiC-42mol%WC)-20vol% Co;
sintered at 1450°C for 120 minutes.
800 X
3.1.5. The Shape of the Sintered Specimens

Apart from shrinkage and minor distortions, all the sintered specimens of all the alloys except VC-Co, retained their cylindrical shape during sintering. The specimens of VC-Co tended to 'flow' and loose their cylindrical shape as sintering proceeded. As will be seen in section 6.5., this can be associated with the low continuity of the carbide grains in this alloy.

3.2. Brief Preview of Microstructural Measurements

Micrographs, representative of the majority of alloys investigated, are shown in Figures 13 to 30.

Growth of the carbide grains occurred during the sintering of all the alloys. The rate of growth varied considerably between different carbides. The grain size distribution, as measured by $d_0/d_1$, tended towards a stationary value as sintering proceeded. In all alloys there existed contacts (i.e. contiguous boundaries) between the grains. The extent of contact was a function of the carbide and the sintering conditions.

The grains of the alloys of TaC, NbC, and combinations of these possessed a cubic shape, modified by rounding of the edges and corners. This shape, observed in two-dimensional microsections in alloys of NbC and TiC in earlier investigations (section 1.2.2.), is now confirmed unequivocally by the scanning electron microscope investigation of the three-dimensional configuration (Figures 18 and 21). This shape is presumably due to the development of ⟨100⟩ crystallographic planes during the growth of the grains (compare Figures 16 and 17). It is distorted by the impingement of neighbouring grains. A tendency to develop these faces was also observed in the TiC-Co alloys (Figure 28) and the HfC-Co alloy. The grain shape in the VC-Co and Mo₂C-Co alloys was near spherical, but flattening of their grain interfaces occurred to allow close packing of the grains as can be seen in Figures 13 and 15. The mixed NbC-VC alloys and the alloy of TiC - 42mol% WC had irregular, ill-defined grain shapes.

Trapped cobalt spheres were observed within the carbide grains of a number of alloys, as shown in Table 15, thus indicating a certain amount of grain coalescence.
3.3. EPMA Studies of the Constitution of Microstructures

The alloys containing mixed carbides were investigated by electron probe micro-analysis to determine the effect of the complex composition of the alloys on the distribution of the constituent elements in their microstructure. The alloy of Mo$_2$C was also investigated, in order to determine the nature of the extra phase observed in its microstructure.

i) The alloys of TaC-NbC and TiC-WC.

When examined optically, both the NbC-TaC and TiC-WC alloys, which nominally contained a single carbide phase, showed evidence of a cored structure in a proportion of their grains, as can be seen in the micrographs, Figures 22, 23, 29, and 30. Such coring has also been observed in TiC-WC-Co alloys by Stjernberg\(^{(41)}\) and by May\(^{(165)}\).

In the present EPMA investigation, it was found that the coring was due to a variation in composition, with a well-defined boundary between the core and the outer layer. The compositions of the cores and outer layers of individual grains in selected specimens are given in Table 16. The cores had a wide range of compositions, in a given alloy, whereas the outer layers had a constant composition. Only a certain proportion of the grains exhibited such coring, and uncored grains usually had a composition close to that of the outer-layer composition.

The results of the analysis can be interpreted as follows: The particles of the original powder had a range of compositions, probably because of incomplete homogenisation during manufacture. During sintering, however, the grain growth processes produce a carbide of constant composition which precipitates onto the original particles. It seems reasonable to suppose that this composition approximates to the equilibrium composition for the system at the temperature of sintering. This equilibrium composition of the solid is shifted, relative to the overall composition of the carbide, towards the component carbide with the lower solubility in the binder phase (see solubility values, Table 21). This implies that the ratio of the constituent carbides, dissolved in the liquid, is shifted towards the constituent with the higher, individual solubility. Thus at equilibrium, the ratio of the carbides in the liquid and in the solid are different. This is quite consistent with the thermodynamic principles of phase equilibria.

The constancy of composition of the growing phase provides support
TABLE 16  The analysis of the microstructure of alloys of NbC-TaC and TiC-WC with Co, using EPMA

<table>
<thead>
<tr>
<th>Carbide in alloy, composition wt%</th>
<th>Nominal overall composition, wt%</th>
<th>Composition of core, wt%</th>
<th>Composition of outer layer, wt%</th>
<th>Composition of binder, wt%</th>
<th>Sintering Time, min.</th>
<th>Temp. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nb</td>
<td>Ta</td>
<td>Nb</td>
<td>Ta</td>
<td>Nb</td>
<td>Ta</td>
</tr>
<tr>
<td>NbC - 10 TaC</td>
<td>80</td>
<td>9.5</td>
<td>n.d.</td>
<td>1 - 10</td>
<td>74 - 71</td>
<td>17 - 20</td>
</tr>
<tr>
<td>NbC - 75% TaC</td>
<td>21.5</td>
<td>71</td>
<td>49 - 7</td>
<td>43 - 86</td>
<td>21 ± 1</td>
<td>70 ± 1</td>
</tr>
<tr>
<td>TiC - 50 WC</td>
<td>40</td>
<td>47</td>
<td>40 - 20</td>
<td>50 - 70</td>
<td>49 ± 2</td>
<td>42 ± 2</td>
</tr>
<tr>
<td>TiC - 70 WC**</td>
<td>24</td>
<td>66</td>
<td>n.d.</td>
<td>n.d.</td>
<td>26</td>
<td>58</td>
</tr>
</tbody>
</table>

* No EMPA corrections carried out for this phase.

** The microstructure was too fine for accurate analysis.
for the principles of composition constraint, applied by Oriani, Li, and Feingold, to solution-reprecipitation growth processes, as discussed in section 1.2.1.4.4.

ii) The alloys of NbC-VC.

The results of the analysis of the microstructures of selected specimens of the (NbC-VC)-Co alloys, are presented in Table 17. In contrast to the other mixed-carbide alloys discussed above, there was no evidence of compositional inhomogeneity within the individual grains of these alloys. However, the same shift in the composition of the grains, relative to the overall composition, towards the carbide with the lower solubility in liquid cobalt, was observed. The corresponding inverse shift in the composition of the binder was also observed. In one of the alloys, predicted to have two carbide phases, the microstructure was far too fine to be able to distinguish the two species of grains (alloy (51.5 wt% NbC - 48.5 wt% VC)-Co, Figure 26). In the other, (69 wt% NbC - 31 wt% VC)-Co, the composition of the majority of grains, as measured by EPMA, was in good agreement with that predicted for the NbC-rich phase from the phase diagram of Kieffer(15). There were few grains of any other composition, and it can be seen that these had a measured Nb content, considerably higher than that predicted for the VC-rich phase. The difficulty in finding grains of this phase is attributed partly to fact that they were probably exceedingly fine, having been precipitated from a higher-temperature state (section 2.1.3.2.ii); and partly to the shift in the solid carbide composition towards NbC, due to the preferential solubility of VC in the liquid.

The preferential solubility of VC in the liquid also explains the presence of the precipitate observed in the binder phase of the alloy, (82 wt% NbC - 18 wt% VC)-Co; this probably is a precipitate of the VC-rich phase, formed during cooling. The proportions of V and Nb in the binder phase are consistent with this explanation.

iii) The alloy of Mo2C

The results of the EPMA analysis of a specimen of the Mo2C-Co alloy are summarised in Table 18.

The theoretical molybdenum content of Mo2C is approximately 94% wt%, and therefore the present analysis indicates a slightly higher than theoretical carbon content. The phase relationships in the Mo-C system are quite complex(3), and a phase with such a carbon content might.
<table>
<thead>
<tr>
<th>Carbide in alloy, composition wt%</th>
<th>Nominal overall composition, wt%</th>
<th>Composition of carbide grains wt%</th>
<th>Composition of binder phase, wt%</th>
<th>Sintering conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nb &amp; V</td>
<td>Nb &amp; V</td>
<td>Nb &amp; V</td>
<td>Time, min. Temp. °C</td>
</tr>
<tr>
<td>NbC 82 - VC 18</td>
<td>73 &amp; 15</td>
<td>77.5 &amp; 11.25</td>
<td>3 &amp; 9</td>
<td>250 &amp; 1450</td>
</tr>
<tr>
<td>NbC 69 - VC 31</td>
<td>68.5 &amp; 18.5</td>
<td>66 &amp; 20.3</td>
<td>5 &amp; 9</td>
<td>385 &amp; 1380</td>
</tr>
<tr>
<td>Phase I</td>
<td>32 &amp; 52</td>
<td>50 &amp; 32.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phase II</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NbC 51 1/2 - VC 48 1/2</td>
<td>45.5 &amp; 40</td>
<td>45 &amp; 36</td>
<td>n.d. n.d.</td>
<td>360 &amp; 1450</td>
</tr>
<tr>
<td>(2 carbide phases)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NbC 29 1/2 - VC 70 1/2</td>
<td>26 &amp; 58</td>
<td>31 &amp; 54</td>
<td>3 &amp; 7</td>
<td>180 &amp; 1380</td>
</tr>
</tbody>
</table>

* EPMA corrections not carried out for this phase

** Composition predicted by the phase diagram of Kieffer (15)

*** Average value for two phases together; the grains were too fine for accurate analysis.
TABLE 18 The analysis of the microstructure of the Mo₂C - 20vol% Co alloy, sintered at 1380°C for 120 minutes

| Carbide grains composition, wt% | Extra, intergranular phase composition, wt% | Binder phase eutectic composition, wt% *
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>Co</td>
<td>Mo</td>
</tr>
<tr>
<td>92.3</td>
<td>0.5</td>
<td>64</td>
</tr>
</tbody>
</table>

*Counts taken from a line scan to give average composition (see section 2.4.)

exist. The result could possibly be due to error in the analysis. The apparent presence of cobalt in this phase is unexpected and was not reported in the recent study of the 1000°C section of the Mo-Co-C system, by Fraker and Stadelmaier (13).

The composition of the extra phase corresponds closely to an Mo₃Co₃C compound, with the approximate formula Mo₃Co₃C. The investigation by Fraker and Stadelmaier showed that this compound forms if the carbon content falls from the Mo₃C-Co, two-phase section, even very slightly. Their investigation also showed that this compound could exist in the composition range, Mo₄Co₂C to Mo₃Co₃C, so an exact equivalence of Mo and Co atoms need not necessarily be expected from the analysis.

The high molybdenum content of the binder phase in this alloy is an indication of the high solubility of the carbide in liquid cobalt during sintering. It is probable that the γ-phase compound precipitated from the liquid phase during cooling, and did not, therefore, interfere with the processes of microstructural development. This is indicated by the appearance of the microstructure.

3.5. Measurement of Interfacial Energies and of Wetting

i) The groove angle, \( \psi \).

The values of the thirteen different groove angles, measured on the specimen of NbC annealed at 1500°C, ranged from 146° to 159°. The variation may be attributed to the variation in relative orientation of the grain pairs that formed the groove boundaries, as well as to experimental errors. The mean value of \( \psi/2 \), given by these angles, is 77.2°, and the median value is 78°. With equation (38), (page 70),
this yields a value for the ratio:

\[ \frac{\gamma_{ss}}{\gamma_{sv}} = 0.415 \]

This is very close to the values for uranium carbide, and conforms to the empirical rule for metals, which predicts values between about 0.25 and 0.5. No other values for carbides are available, and for the purposes of this study, it will be assumed that the ratio is about 0.4 (i.e. 0.3 to 0.5) for all the carbides. Fortunately, the values of the interfacial energies, which are derived from it by the multiphase equilibrium method, are found not to be excessively sensitive to its exact value.

ii) The angle of contact, \( \theta \).

The angles of contact of liquid cobalt on certain carbides, measured in this investigation, are given in Table 19, together with values determined under similar experimental conditions in other investigations. There is quite satisfactory agreement.

The results for NbC indicate that the change in temperature from 1400\(^\circ\)C to 1500\(^\circ\)C does not produce a significant change in \( \theta \), relative to the experimental scatter.

For the purposes of the calculation of interfacial energies, the \( \theta \) values of this investigation were used, if available; otherwise the values of Ramqvist were used, with the assumption that there is not a significant change with temperature. For NbC, the value of \( \theta \) was taken as 11.10.

iii) The dihedral angle, \( \phi \).

The dihedral angle distributions of selected specimens are shown in Figure 49 (page 169). These distributions and the values of \( \phi \) are discussed further in section 6.4.1. The values of \( \phi \) selected for the calculation of interfacial energies, are included in Table 19.

The grains of TaC, at all temperatures, and of NbC at temperatures below 1550\(^\circ\)C were too angular to make a meaningful determination of a unique value of \( \phi \), and so the values for these cases are estimates only.

iv) The surface and interfacial energies.

Using the method described in section 1.3.4., the values of the surface and interfacial energies of the carbide/cobalt systems were calculated from the above interfacial angles together with the values
TABLE 19 The angle of contact and the dihedral angle for the systems of certain carbides with liquid cobalt

<table>
<thead>
<tr>
<th>Carbide</th>
<th>This investigation</th>
<th>Other investigations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp°C</td>
<td>Θ°</td>
</tr>
<tr>
<td>TiC</td>
<td>1450</td>
<td>26 ± 2</td>
</tr>
<tr>
<td>HfC</td>
<td>1500</td>
<td>n.d.</td>
</tr>
<tr>
<td>WC</td>
<td>1450</td>
<td>n.d.</td>
</tr>
<tr>
<td>NbC</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NbC</td>
<td>1420</td>
<td>11½ ± 1</td>
</tr>
<tr>
<td>NbC</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NbC</td>
<td>1450</td>
<td>n.d.</td>
</tr>
<tr>
<td>NbC</td>
<td>1500</td>
<td>12 ± 1</td>
</tr>
<tr>
<td>NbC</td>
<td>1550</td>
<td>n.d.</td>
</tr>
<tr>
<td>TaC</td>
<td>1450</td>
<td>n.d.</td>
</tr>
<tr>
<td>Mo₂C</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>WC</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TiC-5WC</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>- &quot; -</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TiC-7WC</td>
<td>1450</td>
<td>20 ± 2</td>
</tr>
</tbody>
</table>

TABLE 20 The interfacial energies in certain carbide/cobalt systems

<table>
<thead>
<tr>
<th>Carbide</th>
<th>Temp°C</th>
<th>( \gamma_{ss} ) ergs/cm²</th>
<th>( \gamma_{sv} ) ergs/cm²</th>
<th>( \gamma_{sl} ) ergs/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC</td>
<td>1450</td>
<td>854 ± 200</td>
<td>2135 ± 150</td>
<td>437 ± 120</td>
</tr>
<tr>
<td>HfC</td>
<td>1500</td>
<td>729 ± 200</td>
<td>1823 ± 150</td>
<td>385 ± 120</td>
</tr>
<tr>
<td>WC</td>
<td>1450</td>
<td>925 ± 200</td>
<td>2310 ± 150</td>
<td>464 ± 120</td>
</tr>
<tr>
<td>NbC</td>
<td>1450</td>
<td>943 ± 100</td>
<td>2357 ± 100</td>
<td>497 ± 100</td>
</tr>
<tr>
<td>NbC</td>
<td>1550</td>
<td>929 ± 50</td>
<td>2300 ± 50</td>
<td>482 ± 50</td>
</tr>
<tr>
<td>TaC</td>
<td>1450</td>
<td>928 ± 200</td>
<td>2320 ± 150</td>
<td>471 ± 120</td>
</tr>
</tbody>
</table>
of the surface energy of liquid cobalt, determined by Allen (Table 7, page 55). The results are presented in Table 20. Except for NbC, the uncertainty in the values is derived from the uncertainty in the ratio of $\gamma_{\text{ss}} : \gamma_{\text{sv}}$, which, as explained in i) above, was taken as 0.3 to 0.5. It was not possible to evaluate the interfacial energies for WC and Mo$_2$C, because for these carbides the angle of contact is 0, and therefore equation (26) is no longer valid.

The values of $\gamma_{\text{sl}}$ seem quite plausible for such an interface, and if it is assumed that the liquid cobalt was not excessively contaminated with surface active impurities, in the present study, the values of $\gamma_{\text{sl}}$, $\gamma_{\text{ss}}$, and $\gamma_{\text{sv}}$, can be considered to be quite reliable. The values of $\gamma_{\text{sv}}$ do not agree well with those determined by Livey and Murray, but these were evaluated on the basis of some rather tenuous assumptions. It should also be emphasised that the present values of $\gamma_{\text{sv}}$ apply only to the conditions of the experiment, i.e. to a polished surface, at about 1500°C, in a vacuum of about $10^{-5}$ torr containing cobalt vapour.

3.5. The Solubilities of Carbides in Liquid Cobalt

The solubilities of carbides in liquid cobalt, measured by the methods described in section 2.4, are presented in Table 21, together with values reported by other investigators.

It should be noted that the EPMA value for NbC at 1500°C, includes an addition of 1.3 wt% for primary carbide, precipitated at the liquid/solid interface. This precipitate was easily distinguished from the original substrate, because it was completely pore-free. For the analysis of the 1550°C specimen, this correction was not necessary because a large volume of cobalt was used. It should also be noted that all the EPMA results, given in terms of wt% carbide, were derived from the transition metal contents of the drop, on the assumption that in the solution the C:M$^+$ ratio was the same as in the solid carbide. Such an assumption becomes redundant when the solubilities are given in terms of mols/cm$^3$.

The solubility values of this investigation are in good agreement with the values from other sources. As would be expected, there is a clear relationship between the solubilities and the thermodynamic stabilities of the single carbides (Table 4), especially when the
### TABLE 21 Solubilities of carbides in liquid cobalt

<table>
<thead>
<tr>
<th>Carbide</th>
<th>Temp.°C</th>
<th>This investigation</th>
<th>Other investigations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>EPMA analysis</td>
<td>Metallographic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>wt% mols/cm³ (x10⁻³)</td>
<td>wt% mols/ c.c. (x10⁻³)</td>
</tr>
<tr>
<td>TiC</td>
<td>1360(Te)</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>TiC</td>
<td>1360</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>TiC</td>
<td>1450</td>
<td>7 ± 1 9.0</td>
<td>-</td>
</tr>
<tr>
<td>VC</td>
<td>Tₑ</td>
<td>-</td>
<td>~12</td>
</tr>
<tr>
<td>VC</td>
<td>1450</td>
<td>17²/₃ ± 2 20.7</td>
<td>-</td>
</tr>
<tr>
<td>NbC</td>
<td>Tₑ</td>
<td>-</td>
<td>9</td>
</tr>
<tr>
<td>NbC</td>
<td>1420</td>
<td>9²/₃ ± 2 7.2</td>
<td>11</td>
</tr>
<tr>
<td>NbC</td>
<td>1500</td>
<td>12²/₃ ± 2 9.3</td>
<td>11.2 ± 1</td>
</tr>
<tr>
<td>NbC</td>
<td>1550</td>
<td>14²/₃ ± 2 11.0</td>
<td>-</td>
</tr>
<tr>
<td>TaC</td>
<td>1402(Tₑ)</td>
<td>-</td>
<td>13 5.7</td>
</tr>
<tr>
<td>TaC</td>
<td>1420</td>
<td>-</td>
<td>14.5 6.7</td>
</tr>
<tr>
<td>Mo₂C</td>
<td>~Tₑ</td>
<td>~38*</td>
<td>-</td>
</tr>
<tr>
<td>WC</td>
<td>1330(Tₑ)</td>
<td>-</td>
<td>155</td>
</tr>
<tr>
<td>WC</td>
<td>1450</td>
<td>-</td>
<td>50 25</td>
</tr>
<tr>
<td>WC-30TiC (wt%)</td>
<td>1450</td>
<td>~15**</td>
<td>-</td>
</tr>
</tbody>
</table>

*Value obtained from binder phase in a sintered compact (section 3.3.)*

**Value based on the analysis for W, assuming carbide composition is the same in the liquid as in the solid.*
solubilities are expressed in terms of mols/cm$^3$.

It is of interest to note that the solubility of the mixed carbide, WC-30wt% TiC, is almost as low as that of TiC, and much lower than that of WC. This suggests that, in a mixed carbide, the solubility is determined largely by the solubility of the constituent with the lower solubility.
CHAPTER 4

STUDIES OF THE CARBIDE GRAIN GROWTH

4.1 Experimental Results

The results of the present study of the growth of the carbide grains in all the investigated alloys, are presented with the discussions of Chapter 1 in mind.

4.1.1. Isothermal Growth of the Single Carbide Alloys

It was found that the growth of the carbide grains in all the single carbide alloys, could be expressed by a growth equation of the form:

\[ \bar{d}^n - \bar{d}_0^n = K_d t \]

where \( n \) was invariably close to 3, regardless of the growth rate (i.e. the value of \( K_d \)). For this reason, the results of the growth measurements, presented in Figures 31 - 35, are given in the form of plots of \( \bar{d}^3 \) vs. sintering time, in order to give straight lines. Values of the rate constants, \( K_d \), given by the slopes of these plots are given in Table 22, together with values of \( K_d \) calculated with the expression:

\[ K_d = \bar{d}^3 - \bar{d}_o^3 / t \]  \hspace{1cm} (40)

for two different sintering times, \( t \). The degree of agreement of the three values is an indication of the closeness of fit of the results to the equation. Also included in the Table are values of \( K_r \), calculated from the expression:

\[ K_r = \bar{d}^2 - \bar{d}_o^2 / t \]  \hspace{1cm} (41)

for two different times. These values give the rate constants which would produce the observed grain size if the growth were described by the interface-reaction control equation. These values are included in order to allow comparison with theoretically-predicted growth constants, to be discussed later (section 4.2.2.). They also serve to demonstrate how the difference between the closeness of fit of the
observed results to the two growth equations, becomes less definite as the growth rate decreases. Indeed, the growth rate of HfC was so small that the experimental scatter in the values of \( \bar{d} \) masked the difference completely.

To obtain more precise values of \( n \), the \( \bar{d}^3 \) vs. \( t \) plots were extrapolated back to the \( t \)-axis to obtain the hypothetical time, \( t_0 \), for which \( \bar{d} = 0 \); and the origin of the plots was then redefined as the point \( t_0 \), \( \bar{d} = 0 \), thus making valid the equation:

\[
\bar{d}^n = K_d t \quad (n \approx 3)
\]

Therefore, with the new axis, the results could be plotted as log \( \bar{d} \) vs log \( t \), to give straight lines with slopes of \( 1/n \). The values of \( n \), derived in this way, are included in Table 22. They all lie between 2.8 and 3.3. Thus, in terms of the \( n \) values, the observed growth behaviour of the single carbide alloys is that of a process controlled by diffusion through the liquid. However, the nature of the growth cannot be reliably judged on the value of \( n \) alone, and all aspects of the growth behaviour must be considered, as will be shown in the following sections.

It is somewhat difficult to make comparisons of the present results with those of other investigations, because of the differences in experimental conditions and alloy compositions. However, the results for the NbC-Co alloys are in very good agreement with the earlier investigations of this system\(^{(39)}\) (Table 5), which were carried out in similar conditions.

In the present work, the growth in the WC-Co alloy was not studied closely, because this system has been so fully investigated already. It was confirmed, however, that the growth in this system is extremely slow (see Table 15(a)).

4.1.2. The Effect of Temperature on the Growth in Single Carbide Alloys

4.1.2.1. Apparent Activation Energies

The effect of temperature on the growth of the carbide grains in the single carbide alloys, is demonstrated in Figures 31 - 35. On the assumption of section 1.2.1.3.4., that the growth rates should increase exponentially with temperature, the effect of temperature on the growth rate constants is expressed as an Arrhenius diagram in Figure 36.
<table>
<thead>
<tr>
<th>Carbide</th>
<th>Sintering Temp. $T^\circ$C</th>
<th>$K_d$ cm$^3$/sec, $x 10^{12}$</th>
<th>$n$</th>
<th>$K_d = \frac{(\bar{d}^3 - \bar{d}_0^3)}{t}$, $x 10^{12}$</th>
<th>$K_n = \frac{(d^2 - d_0^2)}{t}$ cm$^2$/sec, $x 10^{12}$</th>
<th>$Q$ kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC</td>
<td>1450</td>
<td>$0.0145 \pm 0.001$</td>
<td>3.14</td>
<td>0.0166</td>
<td>0.0145</td>
<td>24.02</td>
</tr>
<tr>
<td>TiC</td>
<td>1500</td>
<td>$0.0354 \pm 0.001$</td>
<td>3.10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiC</td>
<td>1550</td>
<td>$0.074 \pm 0.002$</td>
<td>2.96</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiC(L&amp;S)</td>
<td>1450</td>
<td>$0.014 \pm 0.002$</td>
<td>2.98</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HfC</td>
<td>1500</td>
<td>$0.001 \pm 0.0002$</td>
<td>-</td>
<td>0.0015</td>
<td>0.0012</td>
<td>3.32</td>
</tr>
<tr>
<td>VC</td>
<td>1300</td>
<td>$0.23 \pm 0.02$</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VC</td>
<td>1380</td>
<td>$4.38 \pm 0.1$</td>
<td>3.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VC</td>
<td>1450</td>
<td>$6.02 \pm 0.1$</td>
<td>3.03</td>
<td>5.872</td>
<td>6.037</td>
<td>1568</td>
</tr>
<tr>
<td>VC</td>
<td>1500</td>
<td>$8.40 \pm 0.3$</td>
<td>3.06</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NbC</td>
<td>1420</td>
<td>$0.833 \pm 0.03$</td>
<td>3.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NbC</td>
<td>1450</td>
<td>$1.30 \pm 0.05$</td>
<td>3.11</td>
<td>1.274</td>
<td>1.291</td>
<td>580</td>
</tr>
<tr>
<td>NbC</td>
<td>1500</td>
<td>$2.68 \pm 0.2$</td>
<td>3.19</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NbC</td>
<td>1550</td>
<td>$4.41 \pm 0.2$</td>
<td>3.08</td>
<td>4.41</td>
<td>-</td>
<td>1168</td>
</tr>
<tr>
<td>TaC</td>
<td>1420</td>
<td>$0.04 \pm 0.001$</td>
<td>3.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TaC</td>
<td>1450</td>
<td>$0.066 \pm 0.003$</td>
<td>3.03</td>
<td>0.0657</td>
<td>0.0680</td>
<td>76.53</td>
</tr>
<tr>
<td>TaC</td>
<td>1500</td>
<td>$0.122 \pm 0.004$</td>
<td>3.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TaC</td>
<td>1550</td>
<td>$0.245 \pm 0.007$</td>
<td>3.27</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo$_2$C</td>
<td>1340</td>
<td>$2.7 \pm 0.1$</td>
<td>3.0</td>
<td>2.713</td>
<td>2.747</td>
<td>930</td>
</tr>
<tr>
<td>Mo$_2$C</td>
<td>1380</td>
<td>$3.4 \pm 0.1$</td>
<td>2.8</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
FIGURE 31  The growth of TiC and HfC grains in alloys with 20 vol% Co, during liquid-phase sintering.
( + = carbide supplied by L & S Metallurgical Company, and had a very wide particle size distribution)
FIGURE 32 The growth of VC grains in alloys with 20 vol.% cobalt, during liquid-phase sintering.
FIGURE 33 The growth of NbC grains in an alloy with 20 vol% Co, during liquid-phase sintering.

FIGURE 34 The growth of TaC grains in an alloy with 20 vol% Co, during liquid-phase sintering.
FIGURE 35 The growth of Mo$_2$C grains in an alloy with 20 vol% cobalt, during liquid-phase sintering.
The effect of temperature on the rate of growth of the carbide grains in alloys with 20 vol% Co, during liquid-phase sintering.
In Table 22 are included the 'activation energies', derived from the Arrhenius plots. The implications of the values of these constants will be discussed in later sections. It may be noted, however, that they are in quite good agreement with those of other investigations (see Table 5).

4.1.2.2. The Effect of the Presence of Liquid on Growth

Because the alloy VC-Co exhibited a high rate of carbide grain growth during liquid-phase sintering, it was used to investigate the effect on the growth of passing through the eutectic melting temperature. This is illustrated in Figure 36, in which it can be seen that a sharp change in growth rate occurs. If it is assumed that the effective activation constant, for the growth process below $T_e$, is approximately 100 kcal/mole, then the growth rate at melting increases by a factor of about 5 X. This is a clear indication that the process of growth in the liquid phase involves the transport of material through the liquid.

4.1.3. The Effect of Carbide Composition on its Grain Growth

4.1.3.1. The Effect of Carbon Content

As indicated earlier, in sections 2.1.4. and 3.1.2., the compositions of the single carbides in most of the alloys, was just below the carbon content required to produce free carbon. Consequently, the attempt made to increase the carbon content of the carbide in the NbC-Co alloy, produced traces of graphite at the cobalt/carbide interface, although this may have formed during cooling after sintering.

The effects of the increase in carbon content on the growth behaviour of the carbide, are summarised in Table 23. The addition of carbon produced a marked reduction in the growth rate, which is in keeping with other investigations of cubic carbides (section 1.2.1.5.3.iv), as well as causing a reduction in the activation constant, $Q$.

4.1.3.2. The Growth of Mixed, Solid-solution Carbide Alloys

The growth of the carbide grains in the mixed, solid-solution carbide alloys, (Nb,Ta)C - Co and (Ti,W)C - Co, was similar to that of the single carbide alloys, being described by the growth equation
\[ d^n - d_0^n = K_d t \]

with \( n \) always close to 3. The effect of carbide compositions on the growth rates are summarised in Figure 37 and in Table 24, which also include results from the previous investigation of NbC-based alloys.\(^{(39)}\)

The additions to NbC of the other carbides cause a marked reduction in its growth rate. The detailed study of the NbC-TaC system of alloys, shows that the growth rate is quickly reduced to a rate close to that of TaC, when TaC is added to NbC. Thus, it would appear that the constituent with the lower growth rate becomes rate controlling. This is consistent with the findings of the EPMA study of this system (section 3.3.1), which indicated that the composition of the growing carbide is richer in Ta than the overall composition.

The principle, that the growth is controlled by the constituent with the lower individual growth rate, can be extended to the TiC-WC system of alloys if it is postulated that WC has a dual nature. Thus at small concentrations of WC in TiC, the WC behaves as if it were the constituent with the higher growth rate. As the proportion of WC increases, it takes on the character of the constituent with the lower growth rate. These effects will be shown to have further implications in later sections, in which growth mechanisms are discussed.

4.1.3.3. The Grain Growth in Systems with Two Carbide Phases

The effects of composition on the carbide growth behaviour of alloys in the NbC-VC-Co system are illustrated in Figure 38 and Table 25.

For the alloys in the phase regions of only one carbide phase, the value of \( n \) was again close to 3. In the alloys containing two carbide phases the growth rate was too low to allow an accurate determination of \( n \). No distinction was drawn between the two phases when the grain size was measured, and so the growth constants are average values for the two-carbide phase alloys.

Although the number of alloys in the two-carbide region is insufficient to give a complete quantitative picture, it is clear that the presence of two carbides causes a drastic reduction in the growth rate, beyond that produced by solid solution, in exactly the same way as for oxide systems (section 1.2.1.5.3.). Thus, the exceedingly high value of \( Q \) for the alloy (NbC-\( 43 \) mol\% WC)-Co is due to a change from two to one carbide phases as the temperature is increased.
TABLE 23. The effect of carbon content on the growth behaviour of Niobium Carbide in alloys with 20 vol% cobalt.

<table>
<thead>
<tr>
<th>Carbide</th>
<th>$K_d$ cm$^3$/sec, x $10^{12}$</th>
<th>$n$</th>
<th>$Q$ kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1450°C</td>
<td>1500°C</td>
<td>1550°C</td>
</tr>
<tr>
<td>NbC 0.97</td>
<td>1.3</td>
<td>2.68</td>
<td>4.41</td>
</tr>
<tr>
<td>NbC 0.99</td>
<td>0.92</td>
<td>1.46</td>
<td>2.43</td>
</tr>
</tbody>
</table>

TABLE 24. The effect of its composition on the growth behaviour of the carbide phase in certain mixed carbide alloys with Co

<table>
<thead>
<tr>
<th>Carbide compn. mol%</th>
<th>Rate Constant, $K_d$ cm$^3$/sec, x $10^{12}$</th>
<th>$Q$ kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1420°C</td>
<td>1450°C</td>
</tr>
<tr>
<td>NbC</td>
<td>0.833</td>
<td>1.30</td>
</tr>
<tr>
<td>NbC - 5 TaC</td>
<td>-</td>
<td>0.150 ± .008</td>
</tr>
<tr>
<td>NbC - 16 1/2 TaC</td>
<td>-</td>
<td>0.095 ± .005</td>
</tr>
<tr>
<td>NbC - 62 TaC</td>
<td>-</td>
<td>0.093 ± .004</td>
</tr>
<tr>
<td>TaC</td>
<td>0.04</td>
<td>0.066</td>
</tr>
<tr>
<td>NbC - 10 1/2 TiC**</td>
<td>0.21</td>
<td>-</td>
</tr>
<tr>
<td>NbC - 3 1/2 WC**</td>
<td>0.28</td>
<td>-</td>
</tr>
<tr>
<td>TiC</td>
<td>-</td>
<td>0.0145</td>
</tr>
<tr>
<td>TiC - 22 WC</td>
<td>-</td>
<td>0.02 ± .003</td>
</tr>
<tr>
<td>TiC - 42 WC</td>
<td>-</td>
<td>0.003 ± .001</td>
</tr>
</tbody>
</table>

* Determined from two temperatures only

** From reference (39)
TABLE 25 The carbide grain growth behaviour of alloys of NbC-VC - 20 vol% Co

<table>
<thead>
<tr>
<th>Carbide compn. mol%</th>
<th>Growth rate constant, ( K_d ) cm³/sec, ( \times 10^{12} )</th>
<th>Q kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1380°C</td>
<td>1450°C</td>
</tr>
<tr>
<td>NbC</td>
<td>0.55 (extrapolated value)</td>
<td>1.30</td>
</tr>
<tr>
<td>NbC - 27 VC</td>
<td>0.008 ± 0.004</td>
<td>0.021 ± 0.002</td>
</tr>
<tr>
<td>NbC - 43 VC</td>
<td>0.0003 ± 0.0002**</td>
<td>0.008 ± 0.005</td>
</tr>
<tr>
<td>NbC - 61 VC</td>
<td>n.d.</td>
<td>0.000004***</td>
</tr>
<tr>
<td>NbC - 80 VC</td>
<td>0.056 ± 0.004</td>
<td>0.153 ± 0.03</td>
</tr>
<tr>
<td>VC</td>
<td>4.38</td>
<td>6.02</td>
</tr>
</tbody>
</table>

* Determined from the two temperatures only

**NbC-rich phase + small proportion of VC-rich phase

***Large proportion of both phases present
FIGURES 37 and 38  The grain growth rates of mixed carbides in alloys with 20 vol% cobalt, during liquid-phase sintering.
4.1.4. The Effect of Cobalt Content (Liquid Content) on Grain Growth

The effect of cobalt content on the carbide growth rates in the alloys of TaC and VC is given in Table 26, and is also illustrated in Figure 41, a) and b). (page 146)

<table>
<thead>
<tr>
<th>TABLE 26</th>
<th>The effect of cobalt content on the carbide grain growth rate in alloys of TaC and VC, during liquid-phase sintering</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt content, Kd cm³/sec, x 10¹²</td>
<td>Cobalt content, Kd cm³/sec, x 10¹²</td>
</tr>
<tr>
<td>---------------------------------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>TaC</td>
<td>VC</td>
</tr>
<tr>
<td>---------------------------------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>0.069</td>
<td>0.066</td>
</tr>
<tr>
<td>0.129</td>
<td>0.063</td>
</tr>
<tr>
<td>0.178</td>
<td>0.066</td>
</tr>
<tr>
<td>0.277</td>
<td>0.055</td>
</tr>
<tr>
<td>0.07</td>
<td>10.33</td>
</tr>
<tr>
<td>0.12</td>
<td>8.20</td>
</tr>
<tr>
<td>0.153</td>
<td>7.12</td>
</tr>
<tr>
<td>0.178</td>
<td>6.02</td>
</tr>
</tbody>
</table>

For VC-Co the growth rate increases with decreasing cobalt content, as is to be expected for the growth process controlled by diffusion through the liquid phase. For TaC-Co, however, the growth is almost insensitive to the cobalt content. The implications of this are discussed in section 4.2.3.2.

4.1.5. The Grain Size Distribution of the Carbide

Because none of the alloys exhibited ideal grain shape, it was not possible to derive a distribution of grain sizes, sufficiently accurate to make a useful comparison with the theoretical distributions derived by Wagner (see section 2.2.2.v). This was found to be true, even for alloys of VC and Mo₂C which probably exhibited the most rounded carbide grain shape.

Values of \( \frac{d_m}{d} \), for different sintering times at 1450°C, for single carbide alloys, are given in Table 27. For the reasons given in section 2.2.2.v the values of \( \frac{d_m}{d} \) are probably slightly too low in the case of TaC and NbC, and perhaps too high in the case of TiC which had the most
irregular grain shape.

In general, the results are in qualitative agreement with the theoretical predictions of Wagner (section 1.2.1.3.1.), that the distribution changes to a steady state, and that the time taken to reach this state (τ_D or τ_R) is an inverse function of the grain growth rate.

The ratio, d_m/d_a, for VC and Mo2C are close to the theoretical value for diffusion controlled growth (1.5), whereas for the other carbides it is close to 2.25, the predicted value for interface reaction controlled growth. It must be remembered, however, that the microstructure of these alloys are removed from the ideal system of dispersed particles, proposed by Wagner, and therefore that their grain size distribution will not necessarily be the same.

The distributions for the mixed carbide alloys behaved in a similar manner to those of the single carbides, although the distribution widths in the (Ti,W)C-Co alloys were unusually large (Table 15).

4.2. Theoretical Interpretations of the Results

4.2.1. Observations Relating to the Coalescence Hypothesis

4.2.1.1. The Presence of Cobalt Spheres

As pointed out in section 1.2.1.1., the presence of cobalt spheres, trapped within carbide grains, is an indication of grain coalescence. Cobalt spheres were observed in many of the alloys (e.g. in Figures 17, 20, and 23), and values of their relative frequency (no./unit area) are given in Table 15.

An important observation was that the frequency of spheres in a given alloy did not increase with sintering time. This strongly suggests that they were formed in the first minutes of sintering, i.e. during the re-arrangement process. Further evidence of this is that the frequency of spheres was greatest in those alloys with a cubic grain shape (Table 15). It was shown in section 1.1.4. that, during the re-arrangement process, flat faces on adjacent grains tend to be brought together. If these faces are of the same habit, the probability of instantaneous coalescence is, therefore, increased.

The relative extent of coalescence of this type, can be judged by estimating the fraction of grains in the microstructure which contain
TABLE 27 The ratio of the maximum particle size to the mean particle size in alloys of single carbides with 20 vol% cobalt

<table>
<thead>
<tr>
<th>Carbide</th>
<th>Temp. °C</th>
<th>Ratio $d_m/d$, at sintering time, t, minutes</th>
<th>$\tau_D$ mins.</th>
<th>$\tau_R$ mins.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>TiC</td>
<td>1550</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TiC</td>
<td>1550</td>
<td>4.4</td>
<td>4.3</td>
<td>-</td>
</tr>
<tr>
<td>HfC</td>
<td>1500</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>VC</td>
<td>1450</td>
<td>2.8</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>NbC&lt;sub&gt;0.97&lt;/sub&gt;</td>
<td>1450</td>
<td>2.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NbC&lt;sub&gt;0.97&lt;/sub&gt;</td>
<td>1550</td>
<td>2.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TaC</td>
<td>1450</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TaC</td>
<td>1550</td>
<td>3.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mo&lt;sub&gt;2&lt;/sub&gt;C</td>
<td>1380</td>
<td>1.6</td>
<td>-</td>
<td>1.5</td>
</tr>
</tbody>
</table>

*Times required to reach steady state distribution; predicted by the theory of Wagner for diffusion—and interface-reaction controlled processes, respectively.*
spheres, as follows.

If the frequency of spheres is $N_{As}$ per unit area, then, assuming that no sphere shares a grain with another sphere, the number of grains containing a sphere will also be $N_{As}$. For spherical grains of radius, $r$, the number per unit volume is:

$$N_v = \frac{N_{As}}{2r}$$

Thus for an alloy with a particle radius of 3 microns, and with 200 cobalt spheres/mm$^2$, the number of grains which contain spheres is approximately $3 \times 10^4$/mm$^3$. The total number of grain sections in such an alloy has been found to be approximately $5 \times 10^4$/mm$^2$, which is equivalent to about $10^7$/mm$^3$. Thus about 1 grain in 300 would contain a cobalt sphere. In fact it was found that many grains contain more than one of the spheres and, therefore, this proportion represents an upper limit.

4.2.1.2. The Relationship between Wettability (Contiguity) and Growth

In Figure 39, growth rate constants at 1150°C are plotted against the carbide contiguities for single and mixed carbides. It is clear that there is a general tendency for the growth rate to decrease with increasing contiguity. Since the contiguity at a given binder content is an inverse measure of the wetting in the microstructure (section 1.2.3.1.), this result is opposite to that predicted by the coalescence hypothesis. The same effect was observed by Buist et al. in oxide systems (76).

It may not be concluded from these results, however, that there is a direct relationship between the growth and the contiguity, since changes in alloy composition are also involved. If such a relationship does exist, it appears most likely that contiguity inhibits rather than enhances grain growth.

4.2.1.3. Coalescence versus Solution-Reprecipitation Processes

Reasons why coalescence would not be expected to contribute significantly to grain growth during liquid-phase sintering, have already been discussed in section 1.2.1. In support of these, results so far presented in this study strongly suggest that a process of solution and reprecipitation, and not coalescence, is predominant in producing grain growth during liquid-phase sintering. These results can be summarised:
FIGURE 39  The relationship between the grain growth rate and the contiguity of carbides in alloys with 20 vol% cobalt, during liquid-phase sintering.

FIGURE 40  The process of engulfment, by a grain, of a smaller grain with which it is in contact.
i) The cored structure of the grains of the mixed carbides indicates that growth layers build up on existing grains. Grains containing more than one core are rare, which suggests that coalescence is rare. The same conclusion was drawn by Stjernberg in their studies of TiC-WC-Co alloys.

ii) The number of cobalt spheres, trapped within carbide grains does not increase with sintering time, and there is rarely more than one trapped sphere per 300 carbide grains.

iii) Decreasing wettability in the microstructure or increasing the contact between grains, decreases rather than enhances grain growth.

It would therefore appear to be most fruitful to consider the grain growth in cemented carbides in terms of theories based on processes of solution-reprecipitation. Before examining the experimental results of this investigation in terms of such processes, the processes will be considered in greater detail and, in particular, the effect on them of interparticle contact will be analysed.

5.2.2. Models for Particle Growth involving Particle Contact

As a particle grows by a solution-reprecipitation process, it will tend to grow round and engulf smaller particles with which it is in contact, as illustrated in Figure 40. The result of this is that, if a contiguous boundary forms between the grains, it will tend to become curved. That such a process occurs was suggested by Buist et al., and later confirmed experimentally by Stephenson and White for oxide systems. It was also suggested, quite independently, and confirmed in the previous work on NbC-Co alloys. It has been similarly confirmed for a number of alloys in the present investigation, as can be seen for example in Figures 20 and 23. The effect was especially evident in the scanning electron microscope examination of the TaC alloy (see Figure 21).

Since the boundary becomes curved, there will be a driving force tending to move it towards the centre of the smaller grain. The effect of the mobility of such boundaries on the solution-reprecipitation processes will be considered below.

4.2.2.1. The Case when the contiguous boundaries have higher mobility than the solid/liquid interfaces

If the contiguous boundaries have a higher mobility than the
solid/liquid interfaces, then they will keep pace with them, and in terms of the flux of material, the whole surface of the particles can be considered to behave as solid/liquid interface.

To derive growth equations for this situation, the simplified version of the Wagner model, suggested by Sarian and Weart\(^\text{74}\) will be employed:

Consider a particle of radius, \(r\), exchanging material with all neighbouring particles, and let it be assumed that the average radius of these surrounding particles is the same as the average for the entire system, \(\bar{r}\). The equilibrium concentration of solid constituent in the liquid at the surface of the particle is given by equation (6), i.e.:

\[
C_r = C_0 \exp(2 \frac{\gamma_{sl} \Omega}{rRT})
\]  

(43)

The exponent is generally small compared to unity and so can be expressed as a series:

\[
C_r = C_0 (1 + 2 \frac{\gamma_{sl} \Omega}{rRT})
\]  

(44)

Similarly, the average concentration in the surrounding solution is:

\[
\bar{C}_r = C_0 (1 + 2 \frac{\gamma_{sl} \Omega}{\bar{r}RT})
\]  

(45)

If the interface reaction, leading to dissolution, is much slower than diffusion in the liquid, then the equilibrium concentration at the particle surface, \(C_r\), will not be attained. Instead a steady state value \(C_r'\) will be present.

The flux away from the particle, in terms of numbers of molecules will be the product of the concentration gradient, the diffusion coefficient, and the area of interface, i.e.:

\[
\dot{A} = - \frac{(C_r' - \bar{C}_r)}{\delta} D \frac{4\pi r^2}{\delta} (1 - \delta)
\]  

(46)

where \(\delta\) is the average distance to the surrounding particles. The flux across the interface may be considered to be the product of the deviation from equilibrium at the interface, the area of the interface, and the reaction rate constant, \(k_r\), i.e.:
When a steady state is reached, these two fluxes will be equal and so, equating equations (46) and (47) and re-arranging:

\[ \dot{n} = - (C_t - \bar{C}_t) k_r \frac{4\pi r^2 (1 - \alpha)}{k_r \delta + D} \]  \hspace{1cm} (47)

and

\[ \dot{n} = - \frac{4\pi r^2 (1 - \alpha) k_r D (C_t - \bar{C}_t)}{k_r \delta + D} \]  \hspace{1cm} (49)

It is now necessary to distinguish between the cases of the diffusion-controlled process \((k_r \delta \gg D)\), and the interface-reaction controlled process \((D \gg k_r \delta)\).

Case I - Diffusion-controlled growth

When \(k_r \delta \gg D\), equation (49) becomes:

\[ \dot{n} = - \frac{4\pi r^2 (1 - \alpha) D (C_t - \bar{C}_t)}{\delta} \]  \hspace{1cm} (50)

The rate of change of the particle volume, caused by this flux is equal to the product of the area of the interface and the rate of change of radius, thus:

\[ - 4\pi r^2 (1 - \alpha) \dot{r} = - \dot{n} \Omega \]  \hspace{1cm} (51)

Combining equations (50) and (51):

\[ \dot{r} = \frac{- \Omega D (C_t - \bar{C}_t)}{\delta} \]  \hspace{1cm} (52)

The effect of contiguity cancels out because the contiguous boundaries keep level with the solid/liquid interfaces, which implies that the value of \(r\) remains a true measure of the particle dimensions. This would not be the case if the contiguous boundaries were left behind.

Substituting for \(C_t\) and \(\bar{C}_t\) from equations (44) and (45) into (52):

\[ \frac{dr}{dt} = \frac{-2D\Omega^2 \gamma_{sl} C_t}{RT \frac{r \delta}{\bar{r}}} \left( \frac{\bar{r} - r}{\bar{r}} \right) \]  \hspace{1cm} (53)
It is now assumed that the value of $\delta$, the average diffusion distance, is directly related to and close in value to the mean free path of the liquid phase. If for simplicity, $\delta$ is put equal to $I$, then from equations (25) and (32) (pages 53 and 67 respectively):

$$\delta = \frac{l_1}{3(1 - \alpha)(1 - \alpha)}$$  \hspace{1cm} (54)

whence:

$$\frac{dr}{dt} = - \frac{3}{2} \frac{D \Omega^2 \gamma' \sigma_o (1-\sigma)(1-\alpha)}{R T r \bar{r} \alpha \left\{\bar{r} - r\right\}}$$  \hspace{1cm} (55)

To determine how the mean grain size changes with time, it is necessary to know the form of the grain size distribution. If it is assumed that the distribution derived by Wagner is formed then the maximum particle size, $r_m = 3\bar{r}/2$ (section 1.2.1.3.1.), and:

$$\frac{dr_m}{dt} = \frac{9 D \Omega^2 \gamma' \sigma_o (1-\sigma)(1-\alpha)}{8 R T r_m^2 \alpha}$$  \hspace{1cm} (56)

Integrating equation (56):

$$r_m^3 - r_m(t=0) = \frac{27 \gamma' \sigma_o \Omega^2 D \sigma_o (1-\sigma)(1-\alpha)}{8 \alpha R T} . t$$  \hspace{1cm} (57)

and since $r_m = 3\bar{r}/2$:

$$\bar{r}_m^3 - \bar{r}_o^3 = \frac{\gamma' \sigma_o \Omega^2 D \sigma_o (1-\sigma)(1-\alpha)}{\alpha R T} . t$$

$$= \frac{9 K_D (1-\sigma)(1-\alpha)}{8 \alpha} . t$$  \hspace{1cm} (58)

Rewriting equation (58) in terms of the mean intercept length, $\bar{d}$:

$$\bar{d}^3 - \bar{d}_o^3 = \frac{9 K_D (1-\sigma)(1-\alpha)}{8 \alpha} . t = K_d t$$  \hspace{1cm} (59)
Equation (58) is analogous in derivation and in form to that of Sarian and Weart (equation 19), except that it includes the term \((1-G)\), which allows for the geometric effect of particle contact on the inter-particle distance through the liquid.

**Case II - Interface-reaction controlled growth**

When \(D \gg k_r \delta\), equation (49) becomes:

\[
\dot{A} = -4\pi r^2 (1-G)k_r (C_\infty - C_r) \quad (60)
\]

In analogy with the derivation for diffusion-controlled growth:

\[
\frac{dr}{dt} = -\frac{2 \gamma_{sl} \Omega^2 C_\infty k_r}{R T R} \left( \frac{r}{\bar{r}} \right) \quad (61)
\]

Assuming that the particle size distribution derived by Wagner is formed, then \(r_m = \bar{r}/4\), and:

\[
\frac{dr_m}{dt} = \frac{5 \gamma_{sl} \Omega^2 C_\infty k_r}{2 R T r_m} \quad (62)
\]

Integrating equation (62):

\[
r_m^2 - r_m(t=0)^2 = \frac{5 \gamma_{sl} \Omega^2 C_\infty k_r}{R T} t \quad (63)
\]

whence:

\[
\bar{r}^2 - r_0^2 = \frac{80 \gamma_{sl} \Omega^2 C_\infty k_r}{81 R T} t \quad (64)
\]

Equation (64) differs by only a small numerical factor from the equation derived by Wagner (equation (7)). The small difference is a consequence of the fact that in the present derivation a simplified model was proposed, and the implication is that particle contact is predicted to have no effect on interface-reaction controlled growth. It is therefore concluded that the Wagner equation for interface-reaction controlled growth is applicable to systems exhibiting particle contact,
provided that the contiguous boundaries have greater mobility than the solid/liquid interface.

Before such an equation can be applied to cemented carbide systems, it is necessary to have some knowledge of the possible interface reactions involved, in order to estimate the value of $k_r$. Without making any detailed assumptions about the reaction, it can be proposed that it results from an interfacial barrier or diffusion layer, such that:

$$k_r = \frac{D_x}{\delta_r}$$

(65)

where $\delta_r$ is the thickness of the layer and $D_x$ is the coefficient of diffusion for transport across the layer. The nature of such a layer in cemented carbides remains a matter of speculation; the following possibilities may be proposed:

1) That the layer is an intermediate chemical compound formed between the carbide and the binder phase metal. Such a layer has been proposed as a possible explanation for the dissolution behaviour of WC in liquid Co, by Skolnick(90). He argued that the high activation energy of the dissolution process (175 kcal/mole) was consistent with that of diffusion through such a layer.

2) That it is a layer, on the surface of the particle, depleted in one of the constituent atoms of the carbide. In this case, $D_x$ will be that of the diffusion of the depleted atom through the solid layer, with a corresponding activation energy.

3) That it is merely the energy barrier jumped by an atom when leaving or entering the surface. In this case it might be assumed speculatively that $\delta_r$ is approximately equal to the lattice spacing, and that $D_x$ will be that of diffusion along the interface.

The above possibilities will be considered in relation to the experimental results of this and other investigations, in section 4.2.3.

4.2.2.2. The Case when the contiguous boundaries have a much lower mobility than the solid/liquid interface

If the contiguous boundaries move significantly more slowly than the solid/liquid interfaces, then they will become increasingly more curved as the grain growth by solution-reprecipitation continues.
At some stage it is conceivable that the distortion in shape of the larger, growing grains will be sufficient to prevent further reduction in the overall interfacial energy by further growth. The growth will then be controlled by the movement of the contiguous boundaries. The difficulty in analysing this situation is that, until the critical grain distortion has been attained in all the grains, the growth will be a complex combination of growth by a normal solution-reprecipitation process and the growth involving grain-boundary control. The relative proportion of each type of growth will depend partly on the degree of contact between the grains. The quantitative prediction of the growth behaviour, in this situation, would be extremely difficult, as would be the interpretation of experimental observations of such growth. A similar combination of growth processes, having similar consequences, was proposed in an earlier work, although in that case the two types of boundary were assumed to move independently\(^{(39)}\)(section 1.2.1.1.).

For the limiting case of complete grain-boundary control, the solid/liquid interfaces will follow the movement of the contiguous boundaries and the growth will have the characteristics of solid-state grain growth. If the average curvature of the contiguous boundaries is approximately equal to the average radius \(\bar{r}\) of the particles as a whole, then applying the conventional theory of solid-state grain growth (e.g.\(^{(167)}\)):

\[
\frac{1}{r^2} - \frac{1}{r_0^2} = K_G t \tag{66}
\]

where \(K_G\) is a function of \(\gamma_{ss} \Omega D_g/RT\), in which \(D_g\) is the coefficient of grain-boundary diffusion. The activation of such a growth process would be expected to be approximately that of grain-boundary diffusion, which is usually considered to be approximately three quarters that of lattice diffusion\(^{(167)}\). Unfortunately, the values of \(K_G\) are found to be difficult to predict, partly because grain-boundary motion is very sensitive to impurities.

Referring to the work of Ordan'yan and Avgustnik\(^{(130)}\)(section 1.2.6.4.), for the grain growth of solid NbC it is possible to calculate the approximate value of \(K_G\) as \(2 \times 10^{-10}\) cm\(^2\)/sec at 1500°C. The activation energy for the growth, 65.5 kcal/mole, is somewhat less than that reported for the self-diffusion of carbon in NbC, 75 kcal/mole (Table 11).
If the contiguous grains are of different phases, the contiguous boundaries can be considered to be immobile, and the growth of such grains will eventually be stopped completely. It is therefore to be expected that, in a system of two solid phases, the inhibition of the growth of one phase will increase with the volume fraction of the other, and that the overall grain growth will be a minimum when there are equal volumes of the two phases, since at this composition there is a maximum of inter-phase boundaries\(^{148}\). The growth that would occur in such a system would result from a process of solution-reprecipitation at unlocked solid/liquid interfaces. Because the relative amounts of the two solid phases can change with temperature, however, very high, apparent activation constants might be observed.

4.2.2.3. Reprecipitation on Cooling

Before attempting to apply the theoretical expressions for grain growth, derived above, to experimental observations, it is necessary to consider the effect that precipitation from the liquid, during cooling, might have on the difference between the grain size, measured metallographically, and the grain size at the sintering temperature. To estimate this effect, it will be assumed that the precipitation occurs evenly on the surface of all the grains, and does not occur within the binder phase. The estimated effect will therefore represent the largest that is possible.

If the radius of a particle, just before cooling, is \(r\), then its volume is

\[
V_g = \frac{4}{3} \pi r^3
\]

If after cooling, its radius is \(R\), then its volume is

\[
V_g = \frac{4}{3} \pi R^3
\]

If the volume of binder phase associated with the grain is \(V_b\), then:

\[
\frac{V_b}{V_g + V_b} = \alpha \quad \text{and therefore} \quad V_b = \frac{\alpha V_g}{(1 - \alpha)}
\]

If \(v\) is the volume of solid, dissolved in the liquid just before cooling, then the solubility

\[
C = \frac{v}{v + V_b} \quad \text{and therefore} \quad v = \frac{C V_b}{1 - C} = \frac{\alpha C V_g}{(1 - C)(1 - \alpha)}
\]
But since \( V_g = v_g + v \), then \( v_g = V_g - v \);

and therefore:

\[
\frac{4}{3} \pi r^3 = \frac{4}{3} \pi R^3 \left\{ 1 - \frac{\alpha C}{(1-\sigma)(1-\alpha)} \right\}
\]

and:

\[
r = R \left\{ 1 - \frac{\alpha C}{(1-\sigma)(1-\alpha)} \right\}^{\frac{1}{3}}
\]  

(67)

Thus \( r \) is directly proportional to \( R \) and therefore the form of the true growth equation will not be altered by this type of precipitation, although the observed rate constant will be larger than the true rate constant. The apparent increase in rate constant is, in fact, small. For the WC-Co system, in which \( C \) is large, \( K_D \) will be increased by a factor of at most \( 1.09 X \), in alloys containing 20 vol\% liquid.

It should be added that, if the carbide precipitates within the binder phase, there is a risk that the precipitate particles would be counted as normal grains in the course of quantitative measurements. Since such precipitates are very fine, this would tend to make the measured grain size smaller than the true grain size. Such an error is only likely to occur in alloys with a very fine grain size in which it might not be possible to distinguish between the two types of particle.

4.2.3. Comparison of Theory with Experimental Observations

4.2.3.1. Single Carbide Alloys

Using the values of diffusion coefficients, interfacial energies, and solubilities, that were taken from published works or measured experimentally (Chapters 1, 2, and 3), it is possible to calculate the values of the theoretical rate constants predicted by the Wagner equation (equation 8), and the modifications of it, such as that of Saran and Weart (equation 19), and equation (59) derived above. Values of these rate constants for alloys containing 20 vol\% cobalt are compared with the experimental values in Table 28. The values of \( \alpha \), used for the evaluation of \( K_D' \) (equations 19 and 59), were those pertaining to the sintering temperature; i.e. the effects of density and dissolved carbide were accounted for. Similarly, for the constant in equation (59), the values of \( G \) were adjusted for the increased
### TABLE 28
Comparison between the experimental growth behaviour of single carbides in alloys with 20 vol% cobalt, and the theoretical predictions for growth controlled by diffusion through the liquid.

<table>
<thead>
<tr>
<th>Carbide</th>
<th>Temp. °C</th>
<th>( \frac{d_m}{d} )</th>
<th>Rate constant, ( K_d \text{ cm}^3/\text{sec} \times 10^{12} )</th>
<th>Value of ( D ) used to evaluate ( K_d \text{ cm}^2/\text{sec} )</th>
<th>Q kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>( K_d ) exp.</td>
<td>Rate constant predicted by:</td>
<td></td>
</tr>
<tr>
<td>TiC</td>
<td>1450</td>
<td>3.14</td>
<td>2.5</td>
<td>0.0145</td>
<td>1.43</td>
</tr>
<tr>
<td>HfC **</td>
<td>-1500</td>
<td>-</td>
<td>2.3</td>
<td>0.001</td>
<td>1.85</td>
</tr>
<tr>
<td>VC</td>
<td>1450</td>
<td>3.03</td>
<td>1.8</td>
<td>6.02</td>
<td>4.13</td>
</tr>
<tr>
<td>NbC₀.₉₇</td>
<td>1450</td>
<td>3.11</td>
<td>2.0</td>
<td>1.30</td>
<td>2.30</td>
</tr>
<tr>
<td>NbC₁₀.₇</td>
<td>1550</td>
<td>3.19</td>
<td>2.0</td>
<td>4.41</td>
<td>3.12</td>
</tr>
<tr>
<td>TeC</td>
<td>1450</td>
<td>3.03</td>
<td>2.0</td>
<td>0.066</td>
<td>1.05</td>
</tr>
<tr>
<td>Mo₂C **</td>
<td>1380</td>
<td>2.8</td>
<td>1.6</td>
<td>3.40</td>
<td>3.14</td>
</tr>
<tr>
<td>WC ***</td>
<td>1450</td>
<td>-</td>
<td>-</td>
<td>0.0001</td>
<td>~1</td>
</tr>
</tbody>
</table>

\* \( K_d \) is measured in terms of \( \bar{d} \); \( K_d = \frac{64 \pi K_D}{27} \) (\( K_D \) being in terms of \( \bar{F} \)).

**Theoretical value less reliable because of lack of accurate knowledge of solubility; \( C_o \) put equal to 0.01 moles/cc.

***Theoretical values less reliable because of lack of knowledge of \( \gamma_{sl} \) which was put equal to 250 ergs/cm².
value of \( a_i \)(see sections 1.2.3. and 6.1.). The growth of WC was not studied in detail in the present investigation, but experimental rate constants from other investigations have also been included.

There was sufficient solubility data to allow the fairly accurate evaluation of the effect of temperature on the theoretical growth constants for NbC, it being assumed that the activation energy for the diffusion through the liquid was 10 kcal/mole. The predicted value of \( Q \) could then be measured on the Arrhenius diagram, and the plot is included in Figure 36 (page 121). Theoretical values of \( Q \) for the other carbides were determined in a similar manner although, because of the lack of available data, these values must be considered to be less accurate. The predicted values of \( Q \) are included in Table 28.

Within the limits of the scatter of the experimental data, satisfactory agreement is obtained between the theoretical and experimental rate constants of VC, Mo, and NbC. The closest fit to the experimental rates for these three is achieved by equation (59). In view of the uncertainty in some of the data, and the assumptions made in the theoretical derivations, this can only be fortuitous. In the cases of WC-Co and Mo, the agreement between theory and experiment also extends to the values of the activation constant, \( Q \), and to \( \frac{d_m}{d} \).

The rate constants predicted by the theoretical equations for the alloys, TiC-Co, HfC-Co, TaC-Co and WC-Co, are too high by factors which cannot be explained solely by experimental error. Unless, for some reason, the values of the coefficients of diffusion through the liquid (or possibly, for TaC, the value of \( \gamma_{sl} \)) are exceptionally low in these systems, it must be assumed that their grain growth is controlled by a process other than diffusion through the liquid. Further evidence for this is that the activation constants for the growth of these carbides are considerably higher than predicted by the equations for diffusion-controlled growth. In this respect, however, it should be noted that very little is known about the process of diffusion through liquids of complex composition, and it is conceivable that in such systems the activation energy could be higher than that for simple metallic solutions. Evidence for such a view is provided by the results of Povalotskii et al., for the diffusion of Zr and Ti in liquid iron which contained oxygen \(^{129}\)(Table 10).

The high values of \( \frac{d_m}{d} \) for the alloys of TiC, HfC, and TaC also suggest that their growth is not controlled by diffusion through the
liquid, although this cannot be taken as conclusive evidence, because these alloys do not have the ideal particle configuration for which Wagner derived the theoretical distributions.

The alloy NbC-Co is unusual in that its experimental growth rate is consistent with the equations for diffusion control, whereas its growth activation constant and its grain size distribution width are too high. It is quite possible that this alloy is in transition between diffusion-controlled growth and one of the other processes. This view is supported by the fact that the slope of the Arrhenius plot for NbC tends to fall at temperatures above 1500°C (Figure 36).

In view of the poor agreement between some aspects of the observed growth behaviour of some of the carbides, and the theoretical predictions for diffusion controlled growth, the other mechanisms of growth control must be considered.

i) Interface-reaction controlled growth.

The grain size distribution widths in the alloys TiC-Co, HfC-Co, TaC-Co, and possibly NbC-Co, suggest that the grain growth in these alloys might be controlled by a reaction at the solid/liquid interface. To examine the feasibility of this it might be proposed that the reaction at the interface results from the diffusion of one of the constituent atoms of the carbide through a layer on the surface of the carbide, depleted in that atom (see section 4.2.2.1.), as a result of, for example, preferential solution in the liquid. If, however, the values of the diffusion coefficients of carbon in the carbide, given in Table 11, are used to determine the reaction rate constant with the aid of equation (65) (page 137), and subsequently to estimate the rate constants, $K_r$, for grain growth, it is found that the predicted values are orders of magnitude lower than the observed growth constants, even when the layer thickness is put as low as one lattice spacing. Furthermore, the predicted activation constants for the growth are about 10% higher than the experimental values.

A more probable interfacial reaction is, perhaps, that involved in an atom leaving or entering the surface. As pointed out in section 4.2.2.1., in view of the lack of knowledge of such a process, this can be no more than speculation.

A little more is known about the WC-Co system. If it is assumed that the interface reaction for growth is identical with that for
dissolution in this system, then the rate constant for dissolution, determined by Skolnick(90)(section 1.2.6.3.) can be taken as $k_r$. If this constant, and a value of $\gamma_{el}$ of 250 ergs/cm$^2$ are used to evaluate $K_R$ in the Wagner equation (equation 7), then a value of approximately $2 \times 10^{-12}$ cm$^2$/sec is obtained, which is in fair agreement with the experimentally determined values (Table 5). The value of the activation energy for dissolution (175 kcal/mole), however, is somewhat higher than the values of Q for grain growth.

The value of 3 for the exponent, n, observed for the growth of the carbides in this investigation, is at variance with an interface-reaction controlled process, although, as was shown in section 4.1.1., the value for HfC and TiC could not be determined with accuracy, because of their very low growth rates. An interface-reaction controlled process would produce a value of $n = 3$ if an extra factor or factors caused a continuous decrease in $K_R$ as growth proceeded.

ii) Contiguous-boundary controlled growth.

The value of $2 \times 10^{-10}$ cm$^2$/sec for the solid-state grain growth constant, $K_G$, determined experimentally for NbC (section 4.2.2.2.) is quite close to the rate constant for the growth of this carbide during liquid-phase sintering, (i.e. $K_r$), which is approximately $5 \times 10^{-10}$ cm$^2$/sec (Table 22). It must therefore be considered possible that the growth of NbC, during liquid-phase sintering, could be controlled by the movement of the contiguous boundaries. In Table 29 are presented values of $K_G$ for the other carbides, estimated very roughly from the value for NbC, by assuming that $K_G$ varies in proportion to the solid state diffusion coefficient. Also included in the Table are values of Q, predicted by assuming that the activation energy for grain boundary diffusion is 0.75 x that for lattice diffusion. Allowing for the extremely uncertain nature of the predicted constants, their values show fair agreement with the experimental values for TiC-Co, HfC-Co and perhaps TaC-Co, as well as for NbC-Co. The fact that the experimental values of Q for these carbides are higher than those predicted, could be explained by assuming that the growth is only partially controlled by the contiguous boundaries, as was suggested in section 4.2.2.2. With increasing temperature inter-particle contact usually decreases (sections 1.2.3.2. and 6.2.), and so the degree of contiguous
**TABLE 29** Predicted rate constants for contiguous-boundary controlled growth in alloys of carbides with cobalt at ~1450°C

<table>
<thead>
<tr>
<th>Carbide</th>
<th>$K_p$, exptl. $\times 10^{12}$ cm$^2$/sec</th>
<th>$K_q$, predicted $\times 10^{12}$ cm$^2$/sec</th>
<th>$Q$ kcal/mole</th>
<th>Exptl.</th>
<th>Predicted</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC</td>
<td>20</td>
<td>20</td>
<td>99</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>HfC</td>
<td>2.5</td>
<td>0.2</td>
<td>33</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>VC</td>
<td>1300</td>
<td>200</td>
<td>87</td>
<td>65.5*</td>
<td></td>
</tr>
<tr>
<td>NbC</td>
<td>500</td>
<td>200</td>
<td>84</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>TaC</td>
<td>70</td>
<td>2</td>
<td>33</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>Mo$_2$C</td>
<td>800</td>
<td>20000</td>
<td>140</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>WC</td>
<td>0.5</td>
<td>0.002</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Value for solid-state grain growth measured experimentally.*

Boundary control would be expected to decrease and thereby lead to an apparently high activation energy.

A process which involved only partial control by the contiguous boundaries would also explain the observations of section 4.2.1.2, that the grain growth rate tends to decrease with increasing contiguity of the carbide.

In conclusion it must be admitted that the evidence for a process of contiguous-boundary control is circumstantial. Until much more is known, both about solid state grain growth in carbides, and the possible solution and precipitation reactions occurring at the carbide/liquid interface, it is not possible to determine whether grain growth is interface-reaction or contiguous-boundary controlled, in a given system.

### 4.2.3.2. The Effect of Cobalt Content in VC-Co and TaC-Co Alloys

The effect of cobalt content on the grain growth rates in alloys of VC-Co and TaC-Co, predicted by equation (59), is illustrated in Figure 41, where it is compared with the experimentally observed effect. In evaluating the theoretical rate constant, allowance was made for the increase in $\alpha$ caused by carbide dissolved in the liquid at the sintering temperature.

The agreement between theory and experiment for the VC-Co system
FIGURE 4.1 The effect of cobalt content on the growth rate of VC and TaC grains, during liquid-phase sintering.
is excellent, whereas for the TaC-Co system, not only are the values of \(K_d\) in poor agreement but also the predicted relative effect of the cobalt content is not observed. These findings provide further evidence for the fact that the growth of VC in cobalt is controlled by diffusion through the liquid and that the growth of TaC is not.

4.2.3.3. The Effect of Carbide Composition

i) The effect of carbon content.

The little evidence that exists suggests that, with increasing C:M\(^n\) ratio, the solubility of a carbide in a metal such as cobalt decreases. It is therefore to be expected that carbide grain growth, occurring by a solution-reprecipitation process, would also decrease. Furthermore, the diffusion of carbon in the solid carbide also tends to decrease with increasing carbon content (section 1.2.6.1+) so that growth, controlled by the movement of contiguous boundaries and perhaps also by interfacial reactions, would also be expected to decrease. The observed reduction in the growth rate, caused by increasing the carbon content of the NbC-Co alloy of this investigation and of other carbide alloys in previous investigations (section 1.2.1.5.3.), is therefore not unexpected.

It is, however, not possible to explain in terms of these effects the reduction in the growth activation constant of the NbC-Co alloy, that was observed when carbon was added. It is possible that this effect was the result of an increase in carbon content with increasing sintering temperature (see Table 14).

ii) The growth of mixed carbides.

The complexity of alloys containing mixed carbides makes it very difficult to predict their grain growth behaviour quantitatively. Thus, equations such as (21) and (22), which predict the effect of composition constraint, are only applicable to diffusion-controlled growth in ideal systems and cannot allow for the possibility of changes in growth mechanism caused, for example, by changes in the interface reaction or in particle contact. The results of the EPMA investigation of the mixed carbide alloys, discussed in section 3.3., do provide, however, a basis for certain qualitative predictions.

It was found that the carbide phase in a mixed-carbide alloy becomes enriched in the carbide with the lower individual solubility
in the liquid, and consequently it is to be expected that its growth will be influenced by that carbide to a greater extent than the overall composition of the alloy would suggest. Furthermore, since there is a lower proportion of the dominant constituent in the liquid phase than in the solid phase, its availability (i.e. solubility and mobility), rather than that of the other constituent, will determine the rate of growth.

In addition to these segregation effects, it can be considered possible that the two constituent carbides could interact and produce growth behaviour exhibited by neither of them individually; for example, a new interface reaction might be created.

It follows that as the complexity of the alloy is increased, i.e. as the number of different atom species is increased, so the chance that a growth inhibiting process will be introduced, is also increased.

The investigation of the alloys of the (NbC-TaC)-Co system, indicates clearly that the carbide grain growth is dominated by the growth behaviour of TaC. Small additions of TaC concentrate in the solid and the growth rate is reduced to values close to that of pure TaC. The activation constant for the growth remains approximately constant, and there is no evidence of a new growth mechanism being introduced.

In alloys of the TiC-WC system with cobalt, the TiC concentrates in the solid phase, and so small additions of WC are not expected to influence the growth behaviour considerably. This was found to be the case. However, since WC has a lower growth rate than TiC, it would be expected to cause a slight decrease in the growth of the mixed carbide. This was found not to be so at 1450°C, for the carbide containing 22 mol% WC (Figure 37). That the WC causes an increase in growth in this case, can be explained if it is postulated that at low concentrations in a cubic lattice, the WC has the characteristics of a fast-growing carbide, whereas at higher concentrations its slower growth rate characteristics begin to take precedence. At about 42 mol% WC, the WC begins to appear as a separate phase, and therefore a change in growth mechanism might be expected to occur. Such a change would explain the differences of the growth activation constant observed by different investigators, studying this composition range. In the present study, Q was found to be roughly 80 kcal/mole for the alloy.
(TiC-4.2 mol% WC)-Co, whereas Stjernberg observed a value of 120 kcal/mole for an alloy of similar composition (41). A value of 130 kcal/mole was observed by May in a similar alloy which contained small amounts of free WC grains (165).

Within the solid-solution ranges, at both ends of the NbC-VC system, in the alloys with cobalt, the carbide grain growth is reduced considerably, relative to the growth of the single carbides (Figure 38). For small additions of NbC to VC this is partly to be expected, since the NbC concentrates in the solid phase and is expected to impose its growth characteristics onto the system. However, at compositions above about 10 mol% NbC, the growth rate has values below that of pure NbC. This together with the fact that small additions of VC to NbC also reduce the growth rate, suggest that a new growth-control mechanism is introduced into the system. It has been found that the contiguity is increased considerably when these carbides are combined (Figure 48 b), page 167), and therefore, one explanation of the growth behaviour in this system is that an increase in contiguous boundary control is introduced in the mixed carbides.

The growth behaviour of this system in the region of two carbide phases is in complete agreement with the predictions of an interphase boundary locking mechanism, as discussed in section 4.2.2.2. Grain growth practically ceases when considerable proportions of both phases are present.

4.3. General Conclusions of the Studies of Carbide Grain Growth

i) The single carbide alloys.

An important conclusion of the present investigation of grain growth during liquid-phase sintering, is that it occurs by a process of solution and reprecipitation, which involves transport of material through the liquid binder. At the same time, it is concluded that there are a number of possible mechanisms which can control the rate at which this process proceeds.

All the evidence of this investigation shows that the growth of WC and Mo2C in alloys with cobalt is controlled by the diffusion of the carbide through the liquid. This conclusion, in the case of WC, is at variance with that of Exner et al. (79) The latter was based, however, only on observation of the grain size distribution.
FIGURE 42 The grain growth of carbides in alloys with 20 vol% cobalt, presented in terms of the carbide stability.
The results of the present investigation suggest that it is very unlikely that the growth of TiC, HfC, and TaC, in alloys with cobalt, is controlled by diffusion through the liquid. Instead, processes controlled by an interfacial reaction or by the movement of contiguous boundaries, are probably involved. At temperatures between 1100°C and 1550°C, the growth of NbC grains appears to occur by a process which is in transition between such a control mechanism and the diffusion controlled process.

There is much evidence to suggest that growth of WC grains in WC-Co alloys is controlled by a reaction at the carbide/liquid interface. In many respects, however, this system behaves in an unusual manner, as will be shown below.

In spite of the wide range of behaviour in the grain growth of the carbides investigated, a certain pattern in this behaviour can be recognised. This is demonstrated in Figure 42, in which growth rates and values of the growth activation constant are plotted against the heat of formation of the carbide. It can be seen that the growth characteristics form a continuous series, with the exception of those of WC. For those carbides with a thermodynamic stability greater than that of NbC, the growth rate is far more sensitive to the stability than for those with a lower stability than NbC. The diagram supports the proposition that NbC is at a point of transition.

An important fact, revealed by the diagram, is that WC behaves in an untypical manner, both with respect to growth rate and to the value of Q. It is therefore to be suspected that the growth in WC-Co alloys is controlled by a different mechanism from that of the other carbides. These observations provide further support for the suggestion by Skolnick, that the interfacial reaction in this system could be due to the formation of an intermediate compound at the carbide/liquid interface (90) (section 4.2.2.1.). WC readily forms a mixed compound (η-phase) with cobalt, whereas, with the exception of Mo2C, the other carbides do not (sections 1.1.2. and 1.1.5.2.). Such an explanation is also consistent with the observation that, unlike the other carbides, the growth of WC appeared to increase when the carbon content increased (section 1.2.1.5.3.), as well as with its dual nature in alloys of (Ti,W)C-Co, discussed in the previous section.
ii) Mixed-carbide alloys.

In an alloy of a mixed, solid-solution carbide, the grain growth behaviour is determined, to a large extent, by the constituent with the lowest solubility in the liquid binder phase. For this reason and because the introduction of a new growth-control mechanism is also possible, the addition of one or more extra constituent carbides to a cemented carbide is more likely to inhibit than to enhance the growth. In many cases, the observed grain growth behaviour of the mixed carbides supports the suggestion that the growth is controlled by a mechanism involving the movement of contiguous boundaries, although this evidence cannot be considered as conclusive.

If a mixed-carbide alloy contains more than one solid phase, the grain growth is controlled by the presence of immobile interphase boundaries and is considerably reduced relative to the individual growth rates of the constituent phases alone. When relatively large proportions of the different phases are present, grain growth can practically cease.

iii) The implications of the results.

In view of the influence of the carbide grain size on the properties of cemented carbides, discussed in Chapter 1, these results are clearly of significance to the production of such alloys by liquid-phase sintering. They reveal the general nature of grain growth behaviour and so provide a generalised theoretical basis for the prediction and control of grain growth in the development of new alloys. In particular, it has been shown that considerable reductions in the grain growth of a given carbide can be achieved by the addition of other carbides to the alloy, particularly if the addition forms a separate phase.

It is possible that the information obtained in the present study can, to some extent, be applied to the more general problem of the thermal stability of alloys reinforced with carbides, e.g. dispersion-hardened alloys and eutectic composites. In service, at elevated temperatures, the microstructures of such alloys tend to coarsen and there is a consequent deterioration in properties. By a suitable choice of mixed carbides as the reinforcing phase, such degradation could be significantly reduced.
STUDIES OF THE CARBIDE GRAIN SHAPE

5.1 General Identification of the Grain Shape

The shapes of the carbide grains in all the alloys investigated, could be classified into a number of qualitatively definable classes:

i) Cubic, with various degrees of rounding of the edges, and distorted by the presence of contiguous boundaries.

That the grain shape, normally identified in a two-dimensional section, was indeed basically cubic, was confirmed by leaching out the cobalt binder phase and then examining the grains by scanning electron microscopy (SEM). Pictures of NbC and TaC grains, taken by SEM are shown in Figures 18 and 21. The examination by SEM also confirmed the prediction by Sarian and Weart, that the smaller grains in a microstructure of cubic grains are more rounded than the larger ones, and that many are nearly spherical.

The characteristic cubic shape can be explained in terms of the anisotropy of the interfacial energy, the degree of rounding being dependent on the ratio of the interfacial energy on the (100) planes, \( \gamma_{(100)} \), to that on the other planes. This effect is analysed quantitatively in section 5.3., below.

ii) Near spherical or spheroid, distorted by contiguous boundaries or impingement.

A spherical grain shape is expected in the absence of anisotropy of interfacial energy and in ideal growth conditions. In cemented carbides, however, there is insufficient binder phase to allow perfect spheres to form, even if they were close packed. Because of the packing requirements made necessary by full densification, the grains are pushed together and their shape changes at points of impingement. This is clearly demonstrated in Figure 15, (page 97).

A further possible reason for deviation from the ideal shape is that a grain may tend to grow at slightly different rates in different directions, because of variations in the flux of material in the liquid resulting from the variation in size of the surrounding particles.

iii) Irregular, both rounded and angular.

In some specimens, the grains had ill-defined and irregular shapes.
This was to be expected at the start of sintering, when the grains still had the character of the original powder, but was also observed in specimens which had been sintered for long times. Such cases could be attributed to the uneven growth described in ii), or to very low rates of material transport.

The unusual instance of an angular, irregular grain shape, not affected by the sintering time, occurred in the alloy, (NbC-27 mol% VC) -Co, and this is shown in Figure 24 (page 101). In a SEM investigation of this alloy a characteristic shape could not be recognised. The appearance of the grains suggests that more than one set of crystallographic planes were developing during growth.

iv) Triangular prismatic, angular, and distorted by the presence of contiguous boundaries.

This is the characteristic shape of WC grains in WC-Co alloys (section 1.2.2.1.).

The difficulties of choosing a quantitative parameter for the measurement of shape were discussed in section 1.3.3.1.v. It is considered that a suitable measure of grain shape for the range of shapes described above, is the degree of deviation from the pure cube shape. The parameter, $F_A$, defined in section 2.2.2, as the ratio of the area of the (100) interfaces to the total interfacial area, varies between a value of 1 for a pure, unrounded cube, and 0 for a pure sphere or a grain of irregular but completely rounded shape. It has the disadvantage that it does not distinguish between spheres and other completely rounded shapes, nor does it describe different degrees of irregularity. It has the advantage that it can be directly related to the anisotropy of interfacial energy, as will be shown in section 5.3.

5.2. The Effect of Sintering Conditions and Alloy Composition on Grain Shape

At the start of sintering, the carbide grain shape had the irregular characteristics inherited from the original powder, as can be seen in Figures 14, 16, and 19. In most alloys the grains changed to their characteristic shapes within a few minutes of the start of sintering. These shapes are given in Table 30, in the form of a qualitative description, and in terms of the parameter, $F_A$. 
TABLE 30 The grain shape of the carbide in alloys of carbides with Co

<table>
<thead>
<tr>
<th>Carbide in the alloy, compn. mol%</th>
<th>Temp. °C</th>
<th>Carbide grain shape (t &gt; 120 minutes)</th>
<th>Qualitative description</th>
<th>Ratio, F&lt;sub&gt;A&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC</td>
<td>1450</td>
<td>Cubic, very rounded; and</td>
<td>Near spherical</td>
<td>0.13</td>
</tr>
<tr>
<td>TiC</td>
<td>1500</td>
<td>near spherical</td>
<td></td>
<td>0.12</td>
</tr>
<tr>
<td>TiC</td>
<td>1550</td>
<td></td>
<td></td>
<td>0.07</td>
</tr>
<tr>
<td>HfC</td>
<td>1500</td>
<td>As for TiC</td>
<td></td>
<td>0.09</td>
</tr>
<tr>
<td>VC</td>
<td>1450</td>
<td>Near spherical (all temps.)</td>
<td></td>
<td>0.04</td>
</tr>
<tr>
<td>VC - 20 NbC</td>
<td>1450</td>
<td>Near spherical</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>VC - 39 NbC</td>
<td>1450</td>
<td>Irregular, rounded</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>VC - 57 NbC</td>
<td>1450</td>
<td>Irregular, rounded; near sph.</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>VC - 73 NbC</td>
<td>1450</td>
<td>Ill-defined, angular</td>
<td></td>
<td>?</td>
</tr>
<tr>
<td>NbC&lt;sub&gt;0.99&lt;/sub&gt;</td>
<td>1450</td>
<td>Cubic, slightly rounded</td>
<td></td>
<td>0.60</td>
</tr>
<tr>
<td>NbC&lt;sub&gt;0.97&lt;/sub&gt;</td>
<td>1420</td>
<td>Cubic, rounded</td>
<td></td>
<td>0.51</td>
</tr>
<tr>
<td>NbC&lt;sub&gt;0.97&lt;/sub&gt;</td>
<td>1450</td>
<td>Cubic, rounded</td>
<td></td>
<td>0.41</td>
</tr>
<tr>
<td>NbC&lt;sub&gt;0.97&lt;/sub&gt;</td>
<td>1500</td>
<td>Cubic, rounded; near spherical</td>
<td></td>
<td>0.30</td>
</tr>
<tr>
<td>NbC&lt;sub&gt;0.97&lt;/sub&gt;</td>
<td>1550</td>
<td>Cubic, rounded; near spherical</td>
<td></td>
<td>0.27</td>
</tr>
<tr>
<td>NbC - 5 TaC</td>
<td>1450</td>
<td>Cubic, rounded</td>
<td></td>
<td>0.34</td>
</tr>
<tr>
<td>NbC - 18&lt;sub&gt;2&lt;/sub&gt;TaC</td>
<td>1450</td>
<td>Cubic, slightly rounded</td>
<td></td>
<td>0.53</td>
</tr>
<tr>
<td>NbC - 62 TaC</td>
<td>1450</td>
<td>Cubic, v.slightly rounded</td>
<td></td>
<td>0.69</td>
</tr>
<tr>
<td>TaC</td>
<td>1420</td>
<td>Cubic, v.slightly rounded</td>
<td></td>
<td>0.725</td>
</tr>
<tr>
<td>TaC</td>
<td>1450</td>
<td>Cubic, v.slightly rounded</td>
<td></td>
<td>0.69</td>
</tr>
<tr>
<td>TaC</td>
<td>1500</td>
<td>Cubic, slightly rounded</td>
<td></td>
<td>0.61</td>
</tr>
<tr>
<td>TaC</td>
<td>1550</td>
<td>Cubic, rounded</td>
<td></td>
<td>0.52</td>
</tr>
<tr>
<td>Mo&lt;sub&gt;2&lt;/sub&gt;C</td>
<td>1380</td>
<td>Near spherical (also at 1340°)</td>
<td></td>
<td>0.02</td>
</tr>
<tr>
<td>TiC - 22 WC</td>
<td>1450</td>
<td>Cubic, slightly rounded</td>
<td></td>
<td>0.45</td>
</tr>
<tr>
<td>TiC - 42 WC</td>
<td>1450</td>
<td>Irregular, rounded; near sph.</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>WC</td>
<td>1450</td>
<td>Triangular prismatic</td>
<td></td>
<td>-</td>
</tr>
</tbody>
</table>
FIGURE 43  The effect of the ratio of interfacial energies on the shape of grains with developed (100) faces.
Table 30 demonstrates that the rounding of cubic grains increases with sintering temperature, which confirms the results of the qualitative studies of alloys of NbC with cobalt and iron described in section 1.2.2.2.

The increase in carbon content of NbC produced an increase in the sharpness of the cubic shape. A similar effect was observed for TiC-Co alloys in the investigation by Whalen and Humenik (section 1.2.2.2.).

In the mixed-carbide alloys of (Nb, Ta)C-Co, the degree of rounding of the cubes varied continuously with composition between that of pure TaC and that of pure NbC. The addition of VC to NbC destroyed its cubic shape, producing an ill-defined angular grain at low concentrations and a near-spherical shape at compositions richer in VC (Figures 24 - 27). The addition of 22 mol% WC to TiC sharpened its cubic shape, whereas the carbide containing 42 mol% WC had a rounded shape. It is the latter composition that is generally found in commercial alloys and in these this carbide always exhibits a rounded shape.

5.3. The Relationship between Anisotropy of Interfacial Energy and the Grain Shape

5.3.1. Theoretical Analysis

The theorem of Wulff predicts that the equilibrium shape of a crystal is generated by the inner envelope formed by planes whose perpendicular distance from the centre of the crystal is proportional to the surface energy of a similarly orientated plane in the crystal (95)(96).

Since development of only the (100) faces of the grains was observed, it will be assumed, for the purposes of analysis, that the interfacial energies on all planes have approximately the same value ($\gamma$), with the exception of that on the (100) planes ($\gamma_{100}$). Using the Wulff theorem, it is possible to derive the equilibrium shape, expressed in terms of $F_A$ as a function of the relative values of $\gamma_{100}$ and $\gamma$.

Simple geometric analysis shows that when

$$\gamma > \gamma_{100} > \sqrt{\gamma / 2}$$

the equilibrium shape is simply a sphere with six spherical caps cut off, as indicated in Figure 43 a). Then, by definition, $F_A$ is the ratio of the area of the six circular areas (i.e. the (100) faces) to:
the surface area of the sphere minus the curved surface area of the six caps, and plus the area of the six circular areas. The evaluation of this area ratio in terms of $\gamma$ and $\gamma_{100}$ is a matter of fairly straightforward geometry and gives:

$$ F_a = \frac{A_{100} + A_{\text{curved}}}{A_{100}} = \frac{3\gamma^2 - 3\gamma_{100}^2}{6\gamma_{100}^2 - 3\gamma_{100}^2 - \gamma^2} \tag{68} $$

When $\gamma_{100} = \gamma/\sqrt{3}$ the circular areas just impinge and equation (68) still applies.

When $\gamma_{100} < \gamma/\sqrt{3}$ the circular areas overlap and the shape becomes a cube with rounded corners and partially bounded by sharp edges, as indicated in Figure 43 b). The surface area of the (100) faces, in this case, is that of the six circles minus that of twelve segments. The evaluation of this in terms of the $\gamma$ values is, again, reasonably straightforward, and gives:

$$ A_{100} = 6\pi \left( \gamma^2 - \gamma_{100}^2 \right) - 2\gamma \left\{ S(\gamma^2 - \gamma_{100}^2) - \gamma_{100} \sqrt{\gamma^2 - 2\gamma_{100}^2} \right\} \tag{69} $$

where $$ S = \sin^{-1} \sqrt{\frac{\gamma^2 - 2\gamma_{100}^2}{\sqrt{\gamma^2 - \gamma_{100}^2}}} $$

The evaluation of the total area of the shape, however, is somewhat more difficult and involves the double integration of a rather complicated function (168), the result being:

$$ A_{\text{total}} = A_{100} + 4\pi \gamma^2 + 12\pi \gamma \gamma_{100} - 2\gamma Z \tag{70} $$

where

$$ Z = \gamma \left\{ \gamma_{100} \tan^{-1} \frac{\gamma_{100}^2}{\gamma \sqrt{\gamma^2 - \gamma_{100}^2}} + 2 \gamma_{100} \tan^{-1} \sqrt{\frac{\gamma^2 - 2\gamma_{100}^2}{\gamma_{100}^2}} \right\} $$

When $\gamma_{100} < \gamma/\sqrt{3}$, the curved surfaces disappear altogether and the shape is a perfect cube.
In Figure 44, $F_A$, derived with the above equations, is shown as a function of the interfacial energy ratio $\gamma_{100}/\gamma$. It demonstrates that when the ratio is less than $1/\sqrt{3}$, the equilibrium grain shape is a pure cube ($F_A = 1$). As the ratio increases from $1/\sqrt{3}$ to $1/\sqrt{2}$, the cube corners begin to round, but a proportion of sharp edges remains, and a random two-dimensional section would reveal some angular and some rounded corners on the particle sections. When the ratio increases above $1/\sqrt{2}$, all sharp edges disappear and the shape quickly takes on a near spherical appearance.

5.3.2. Correlation between Theory and Experimental Results

At first sight it would appear that the relationships derived above would allow a determination of the anisotropy of interfacial energies in the carbides by the comparatively straightforward measurement of the factor $F_A$, on two-dimensional sections. For example, the value of $F_A$ for NbC-Co at 1500°C is 0.3, which corresponds to a ratio, $\gamma_{100}/\gamma$ of 0.895; similarly the value of the ratio for TaC-Co at 1450°C is found, from the value of $F_A$, to be 0.76. In both cases therefore, no grains in these alloys would be expected to have straight edges. However, the SEM examination of these specimens showed that the TaC grains had well-defined straight edges (Figure 21) and that the NbC grains had traces of straight edges (Figure 18). By measurement of the dimensions of a number of large, well-defined grains in SEM pictures, it was possible to calculate the values of $\gamma_{100}/\gamma$ for TaC-Co as approximately 0.60, and for NbC-Co as approximately 0.70.

Thus the values of $F_A$, measured on a microstructure, are lower than predicted by theory. The reason for this was made clear by the SEM investigation, which showed that the smaller grains in the microstructure are far more rounded than the large grains. The probable explanation for this was discussed in section 1.2.2.2. It must therefore be concluded that the measurement of $F_A$ on a two-dimensional microsection, cannot be used to determine the ratio of $\gamma_{100}/\gamma$ accurately. It is however, a convenient and sensitive measure of the relative degree of shape anisotropy.
FIGURE 44 The effect of the ratio of interfacial energies on the theoretical shape of grains with developed (100) faces.
CHAPTER 6

STUDIES OF THE CONTACT BETWEEN CARBIDE GRAINS

6.1. The Effect of Cobalt Content on Contiguity

Before discussion of the effect of sintering variables or alloy composition on the contact between carbide grains, it is helpful to have knowledge of the influence of the binder-phase content on the carbide contiguity. Studies were made of this effect in alloys of TaC-Co and VC-Co, since these represented alloys with high and low degrees of contact. The results of the studies are presented in Figure 45 and are seen to be in agreement with those of earlier studies of alloys of different carbides (Figure 9, section 1.2.3.). The prediction that the initial sensitivity of $G$ to $\alpha$ (i.e. the value of $-cG/d\alpha$ at low $\alpha$) increases with wettability is confirmed.

6.2. The Effect of Sintering Conditions on Contiguity

As has already been discussed, the cobalt content of individual specimens tended to vary somewhat during sintering. By assuming the $G$ versus $\alpha$ curves for all alloys to be of a similar form to those in Fig. 45, it was possible, by interpolation, to normalise fairly accurately the contiguity values of individual specimens to a value of $\alpha = 0.2$. In this way it was possible to determine the effect of variables, such as the conditions of sintering, independently of $\alpha$.

6.2.1. The Effect of Sintering Time

The effects of sintering time on the contiguity of a number of alloys, at certain temperatures, are shown in Figure 46. In most cases the contiguity tended to fall during sintering towards a constant value. In the alloy HfC-Co, however, the contiguity increased slightly during sintering, while in the TiC-Co alloys it did not change significantly. In all alloys, the contiguity tended towards a constant value at longer sintering times in agreement with the concept of an equilibrium value associated with a balance between the interfacial and contiguous boundary energies, as discussed in section 1.2.3.

With the exception of that of VC-Co, the values of $G$ after 120 minutes of sintering are in good agreement with those of other invest-
gators (Table 6). Values of \( G(\alpha = 0.2, t \geq 120) \) are included in Table 32.

In Table 31, results are presented which show the influence of heating-up time and pre-sintering time on the contiguity of VC at the start of liquid-phase sintering. These demonstrate that some solid-state sintering of the carbide occurs during the heating up of the cemented carbide, and that, if heating up is performed very rapidly, the carbide contiguity at the start of liquid-phase sintering is significantly lower than it is if some pre-sintering is carried out.

Since the initial contiguity is variable and dependent on the previous history of the compact, it follows that the way that contiguity is observed to change during sintering will also be variable. Whether the contiguity increases or decreases with sintering time will depend on the relative values of the initial contiguity and the equilibrium contiguity. This is a possible explanation of the apparent conflict between the results of Gurland and those of Exner and Fischmeister, discussed in section 1.2.3.2.

6.2.2. The Effect of Sintering Temperature

The effect of sintering temperature on the contiguity of the single carbide alloys is shown in Figure 57 and Table 32. In the alloys of VC-Co, NbC-Co, and TaC-Co, the contiguity tends to decrease slightly with increasing temperature. In the latter two alloys the change may be associated with the rounding of their cubic grain shape, which has been

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Time at 1200° mins.</th>
<th>Time above 1000° mins.</th>
<th>Total heating time, mins.</th>
<th>Contiguity ( G(\alpha =0.2, t=0) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>4</td>
<td>25</td>
<td>0.27</td>
</tr>
<tr>
<td>2 (std. treatnt)</td>
<td>5</td>
<td>20</td>
<td>105</td>
<td>0.34</td>
</tr>
<tr>
<td>3</td>
<td>120</td>
<td>130</td>
<td>225</td>
<td>0.35</td>
</tr>
<tr>
<td>4</td>
<td>2h0</td>
<td>260</td>
<td>430</td>
<td>0.35</td>
</tr>
</tbody>
</table>
The effect of cobalt content on the carbide contiguity in the alloys VC-Co and TaC-Co
The change of carbide contiguity during liquid-phase sintering of alloys with 20 vol% cobalt.

The effect of sintering temperature on the carbide contiguity in alloys with 20 vol% cobalt.
<table>
<thead>
<tr>
<th>Carbide compn. mol%</th>
<th>Sinter. Temp°C</th>
<th>G(α=0.2) ± 0.02</th>
<th>Dihedral angle ϕ°</th>
<th>No. of contacts p. grain</th>
<th>Angle of contact θ°</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC</td>
<td>1450</td>
<td>0.25</td>
<td>0.24</td>
<td>25</td>
<td>6.8</td>
</tr>
<tr>
<td>TiC</td>
<td>1550</td>
<td>0.29</td>
<td>0.29</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>HfC</td>
<td>1500</td>
<td>0.32</td>
<td>0.37</td>
<td>37½</td>
<td>40***</td>
</tr>
<tr>
<td>VC</td>
<td>1380</td>
<td>0.34</td>
<td>0.08</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>VC</td>
<td>1450</td>
<td>-</td>
<td>0.08</td>
<td>8</td>
<td>13***</td>
</tr>
<tr>
<td>VC</td>
<td>1500</td>
<td>-</td>
<td>0.05</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>VC - 20NbC</td>
<td>1450</td>
<td>-</td>
<td>0.40</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>VC - 39NbC</td>
<td>1450</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>VC - 57NbC</td>
<td>1450</td>
<td>-</td>
<td>0.43</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>VC - 73NbC</td>
<td>1450</td>
<td>-</td>
<td>0.41</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>NbC 0.99</td>
<td>1450</td>
<td>0.36</td>
<td>0.32</td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td>NbC 0.99</td>
<td>1550</td>
<td>0.30</td>
<td>0.26</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>NbC 0.97</td>
<td>1450</td>
<td>0.32</td>
<td>0.27</td>
<td>4.8</td>
<td>11½</td>
</tr>
<tr>
<td>NbC 0.97</td>
<td>1550</td>
<td>0.30</td>
<td>0.22</td>
<td>16½</td>
<td>11½</td>
</tr>
<tr>
<td>NbC - 5TaC</td>
<td>1450</td>
<td>0.40</td>
<td>0.32</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>NbC - 18½TaC</td>
<td>1450</td>
<td>0.47</td>
<td>0.37</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>NbC - 62 TaC</td>
<td>1450</td>
<td>0.46</td>
<td>0.38</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>TaC</td>
<td>1450</td>
<td>(0.44)</td>
<td>0.36</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>TaC</td>
<td>1550</td>
<td>0.39</td>
<td>0.33</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Mo2C</td>
<td>1340</td>
<td>-</td>
<td>~0.15</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Mo2C</td>
<td>1380</td>
<td>0.40</td>
<td>~0.15</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>TiC - 22WC</td>
<td>1450</td>
<td>-</td>
<td>0.38</td>
<td>4.8</td>
<td>24½**</td>
</tr>
<tr>
<td>TiC - 42WC</td>
<td>1450</td>
<td>-</td>
<td>0.43</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>WC **</td>
<td>1420</td>
<td>(0.5)</td>
<td>0.10</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

*Values in parentheses are extrapolated. **Ref. (37). *** Ref. (112)  
# Ref. (27)
observed (section 5.2.). In the Ti-Co alloy, the contiguity increased with increasing temperature.

The development of G towards a constant value during sintering was observed at all the temperatures investigated.

6.3. The Effect of Carbide Composition on Contiguity

i) The effect of carbon content.

The addition of extra carbon to the NbC-Co alloy increased the contiguity of the carbide, as is indicated in Table 32. It is to be noted that the increase occurs in association with a sharpening of the cubic grain-shape. The significance of this is discussed in section 6.7.

ii) The contiguity of the mixed carbides.

The effect of carbide composition on the contiguity of the carbide grains in the mixed-carbide alloys is shown in Figure 48 a), b) and c), and in Table 32. The change of the contiguity of these alloys with sintering time and temperature was very similar to that of the single carbides and need not be elaborated on.

The effect of the carbide composition on the contiguity appears to be similar, in some respects, to its effect on the grain growth. Thus, additions of a carbide with higher individual contiguity were more effective in increasing the contiguity than additions of a carbide with a lower contiguity were in reducing it. Consequently, small additions of one carbide to another never reduced the contiguity of the latter significantly. The alloys of (NbC-VC)-Co are notable in that the contiguity of all compositions was significantly higher than that of both constituent carbides.

The sensitivity of contiguity to composition is a reflection of its sensitivity to small changes in the relative values of the interfacial energy and the contiguous boundary energy.

6.5. The Relationship between Wettability and Contiguity

6.5.1. The Dihedral Angles of the Single Carbides

The cumulative distributions of apparent dihedral angles of certain specimens are shown in Figure 49. The true dihedral angle was taken as the median value of such a distribution (section 1.3.3.1.(ix), p. 68).

Included in Figure 49 is the theoretical distribution for a unique value of the dihedral angle derived by Harker and Parker\(^{151}\). That the
Carbide contiguity \( (c^* = 0-2, 120 \text{ min}) \)

\[ 167 \]

\[ 0-4 \]

\[ 0-2 \]

\[ 1380^\circ C \]

\[ 1450^\circ C \]

\[ 1450^\circ C \]

\[ 1550^\circ C \]

\[ A \]

0.1

0.2

0.3

0.4

\( \text{NbC} \)

\( 0-5 \)

\( \text{TaC} \)

\( \text{NbC} \)

\( 0-5 \)

\( \text{VC} \)

\( \text{WC} \)

\( 0-5 \)

\( \text{TiC} \)

\( \text{Carbide composition, (mol. fraction)} \)

FIGURE 58 The effect of carbide composition on carbide contiguity, in alloys with 20 vol\% cobalt binder phase.
measured distributions are wider than the theoretical distribution, implies that in the alloys investigated, there exists a range of dihedral angles, probably due to the anisotropy of interfacial energy. The angle distribution for VC-Co specimens extended to values of apparent angles below zero. This means that a thin layer of cobalt was present between certain grains which, it is clear, would have made contact had a finite dihedral angle existed.

In Figure 50 is shown the effect of sintering time on $\phi$, for the alloy VC-Co. In the same way as contiguity, the dihedral angle changed towards an equilibrium value during sintering, an effect which was also observed by Fischmeister et al.\textsuperscript{(70)}(section 1.2.3.2.). Such an effect is to be expected, since the dihedral angle at the start of sintering is inherited from the groove angles, formed between grains and pores by the solid-state sintering that occurs during heating up (section 6.2.1.). The dihedral angles given in Table 32 (and Table 19), were measured on specimens sintered sufficiently long to allow the equilibrium values to be reached.

### 6.4.2. The Relationship between $G$, $\phi$, and $\theta$

Since both the dihedral angle and the contiguity at a given binder phase content, are predicted to be dependent on the ratio of $\gamma_{\text{sl}}$ and $\gamma_{\text{ss}}$, a simple relationship between the two parameters is to be expected. The prediction is confirmed to a good approximation in the alloys of this investigation, as is seen in Figure 51. The relationship is empirically determined as:

$$G(\alpha = 0.2) \approx 0.01 \phi^0$$

These observations confirm that the contiguity may be considered to be an inverse measure of the wettability in the pore-free microstructure, as has already been assumed (e.g. in section 4.2.1.2.).

It is sometimes assumed that the wettability in an alloy microstructure can be related to the wettability measured in terms of the angle of contact in the sessile drop experiment (e.g. see section 1.2.1.2.). The basis for this assumption is probably intuitive rather than theoretical. Examination of the contiguity and angle-of-contact values in Table 32, shows that the assumption is not justified.
FIGURE 49 Cumulative distributions of apparent dihedral angles.

FIGURE 50 The change in dihedral angle during sintering of an alloy of VC with Co.

FIGURE 51 The relationship between contiguity and dihedral angle.
6.5. The Continuity of the Carbide Phase

The continuities of a number of alloys are included in Table 32, expressed in terms of the number of contacts per grain (section 1.3.3.1. vii). The parameters for different alloys cannot be compared with any accuracy because of the limitations of the measurement. It is of interest, however, that the continuity in VC-Co alloys was far lower than that of the other carbides, in their alloys. This is consistent with the finding that the VC-Co specimens did not retain their shape during sintering (section 3.1.4.), a clear indication that the carbide did not form a continuous skeleton. Furthermore, the value for this alloy of 2.2 contacts per grain is in quite good agreement with the critical value of 1.3 - 1.5, predicted by Gurland for the breakdown of complete continuity, (section 1.2.3.). Similarly, the contiguity of the VC-Co alloy was lower than the critical contiguity, 0.16, for the system of silver spheres in bakelite, investigated by Gurland. These observations imply that the carbides in the other alloys formed a continuous carbide skeleton throughout sintering.

6.6. Particle Contact and Densification

The results of the previous section, together with the high values of contiguity, observed in specimens which were sintered for short times, strongly suggest that in the large majority of cemented carbides, the carbide phase is in the form of a continuous skeleton at all stages of sintering. At first sight, this conclusion is at variance with the requirements of the processes of liquid-phase densification, which were discussed in section 1.1.4.2. In particular, it might be argued that a continuous skeleton is inconsistent with a process of re-arrangement. The following model of the densification process shows that this is not necessarily so.

It has been shown that while a compact is being heated up, a certain amount of solid-state sintering occurs, and contiguous boundaries form between the carbide particles. The formation of these boundaries is governed by the relative values of $\gamma_{sv}$ and $\gamma_{ss}$, and, in general, the degree of contact at the onset of liquid-phase sintering will depend on the way the specimen was heated (section 6.2.1.), and also on the solid-state sintering behaviour of the carbide. Upon the formation of the liquid, however, the equilibrium contact between
particles is governed by the relative values of $\gamma_{bl}$ and $\gamma_{ss}$. Many of the contacts formed during heating will therefore become unstable and will begin to be penetrated and broken by the liquid, the process being enhanced by the dissolution of a proportion of the carbide in the liquid. Moreover, other contacts will become unstable as densification progresses as a result of stresses placed on them by the capillary forces (section 1.1.4.). However, at the same time as the old skeleton is being broken down, new equilibrium contacts, governed by the relative values of $\gamma_{bl}$ and $\gamma_{ss}$, will develop. Thus, if observed at any instant in time, the specimen as a whole could appear to possess a continuous solid skeleton although the contacts in the skeleton will be continuously changing from the original set to a new equilibrium set. While the breaking of old contacts continues, single grains and groups of grains will be released locally and so be able to re-arrange themselves before rejoining the skeleton. The re-arrangement process will continue until the majority of the unstable contacts have been broken.

During the 'transient-skeleton' stage of shrinkage, it seems probable that a solution-reprecipitation process of densification, similar to that proposed by Kingery, would be able to occur simultaneously. It is, however, difficult to envisage how such a process could continue after the formation of a stable, permanent skeleton. It is necessary to conclude, therefore, that in the majority of alloys of this investigation, densification occurred mainly during the re-arrangement stage of sintering, which indeed seemed to be the case (section 3.1.1.).

In alloys of high wettability, such as VC-Co, insufficient new contacts will form during the re-arrangement process to maintain a skeleton and the compact will consequently collapse or loose its shape.

6.7. The Relationship between the Degree of Contact and the Grain Shape

In section 1.2.3.1. it was predicted that the contact between the carbide grains should increase with the deviation of particle shape from sphericity. In the present investigation this prediction was confirmed by the fact that the contiguity of the alloys increased as the cubic shape of the grains became less rounded, i.e: when carbon was added to the NbC-Co alloy; with increasing TaC content in the (Nb,Ta)C-Co alloys; and when 22 mol% WC was added to TiC. However, since it is not known to what extent the interfacial energy also changed in these cases, it is not possible to judge the exact effect of the shape.
CHAPTER 7

AN INVESTIGATION OF CERTAIN MECHANICAL PROPERTIES

7.1. The Microhardness of the Carbide Grains

The microhardness of individual carbide grains, measured on those specimens which had grains of sufficient size, is given in Table 33. Apart from the value for VC, the values for the single carbides are in good agreement with recently reported values for carbides with similar carbon contents.

Table 33 The microhardness of carbide grains

<table>
<thead>
<tr>
<th>Carbide (mol%)</th>
<th>Microhardness, $kg/mm^2$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This investigation (load 100 g.)</td>
<td>Other investigations</td>
</tr>
<tr>
<td>TiC</td>
<td>2500 ± 100</td>
<td>2750 (20)</td>
</tr>
<tr>
<td>VC</td>
<td>2300 ± 100</td>
<td>3000 (20)</td>
</tr>
<tr>
<td>NbC (0.99)</td>
<td>1750 ± 50</td>
<td>1800 (20)</td>
</tr>
<tr>
<td>NbC (0.97)</td>
<td>1800 ± 50</td>
<td>1850 (20)</td>
</tr>
<tr>
<td>TaC</td>
<td>1500 ± 50</td>
<td>1450 (20)</td>
</tr>
<tr>
<td>MoC</td>
<td>1280 ± 100</td>
<td>1260 - 1800 (3)</td>
</tr>
<tr>
<td>NbC - 5 TaC</td>
<td>1850 ± 50</td>
<td></td>
</tr>
<tr>
<td>NbC - 18.5TaC</td>
<td>1760 ± 50</td>
<td></td>
</tr>
<tr>
<td>NbC - 62 TaC</td>
<td>1660 ± 50</td>
<td></td>
</tr>
<tr>
<td>VC - 20 NbC</td>
<td>2100 ± 100</td>
<td></td>
</tr>
<tr>
<td>TiC - 22 WC</td>
<td>2215 ± 100</td>
<td>2300 (25)</td>
</tr>
</tbody>
</table>

The effect of composition on the microhardness of mixed carbides of the TaC-NbC system, is illustrated in Figure 52. In view of the uncertainty in the measurement of the microhardness, the detection of a maximum at low TaC contents is barely significant. Analogous maxima have been reported, however, in the systems, TiC-WC (25) and TiC-VC (18).
FIGURE 52 The effect of composition on the microhardness of carbides in the NbC-TaC system.
7.2. The Macrohardness of the Alloys

7.2.1. The Effect of Binder-Phase Content on Hardness

As was indicated in section 1.1.6.1., the binder phase content is probably the most significant single factor to affect the hardness of cemented carbides. In general, this was found to be the case in the present investigation. The effect of the binder-phase content on the hardness of TaC-Co and TiC-Co alloys is shown in Figure 53 in which it can be seen that, as expected, the hardness fell continuously with increasing binder-phase content.

Similar curves for VC-Co and NbC-Co alloys have not been included because the difficulty in the accurate measurement of the hardness of these alloys, mentioned in section 2.6., produced a scatter which masked the effect of cobalt content. Measurements were not attempted on the HfC-Co alloy because of its high porosity, nor on the alloy Mo₆C-Co because of the presence of η-phase.

The results shown in Figure 53 indicate that the hardness of the TaC-Co alloys increased very slightly with decreasing grain size. Nevertheless, within the range of microstructures investigated, any effect of grain size on the hardness of the TaC and TiC alloys can be concluded to be relatively slight and could not be detected with experimental reliability. Similarly, for alloys of a given carbide, the variation in contiguity, at a fixed binder-phase content, was insufficient to allow the independent effect of this parameter on hardness to be detected. However, as will be shown in the following sections, there was a sufficient difference between the microstructures of the alloys of different carbides to produce a measurable effect.

7.2.2. The Effect of the Carbide Phase on the Hardness

The insensitivity of the hardness of alloys of individual carbides to grain size and to contiguity at a fixed binder content made it possible to determine characteristic hardnnesses for alloys of a given binder content. Values for some of the alloys investigated are given in Table 34, and the dependence of the hardness of alloys (for α = 0.2) on the hardness of their constituent carbides is shown in Figure 54.

Figure 54 demonstrates that the overall hardness of an alloy is not merely a function of the hardness and relative proportions of its constituent phases, but also depends on its microstructural properties.
FIGURE 53 The effect of binder phase content on the hardness of TaC-Co and TiC-Co alloys.
<table>
<thead>
<tr>
<th>Carbide compn.,mol%</th>
<th>Macrohardness $\text{kg/mm}^2$</th>
<th>Microhardness of carbide, $\text{kg/mm}^2$</th>
<th>Resistance to cracking, $W$, $(d &gt; 5\mu)$ $\text{kg/mm}$</th>
<th>Range of microstructural parameters for which hardness and $W$ values are valid</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC</td>
<td>1050 ± 25</td>
<td>2500</td>
<td>300 ± 20</td>
<td>$0.25 - 0.29$, $4 - 8$, $1.5 - 3$</td>
</tr>
<tr>
<td>WC</td>
<td>975 ± 100</td>
<td>2300</td>
<td>220 ± 20</td>
<td>$0.10 - 0.15$, $15 - 40$, $4 - 10$</td>
</tr>
<tr>
<td>WC - 20 NbC</td>
<td>1150 ± 50</td>
<td>2100</td>
<td>100 ± 20</td>
<td>$\sim 0.42$, $6 - 12$, $2.5 - 5$</td>
</tr>
<tr>
<td>WC - 39 NbC</td>
<td>$\sim 1400$</td>
<td>$-$</td>
<td>50 ± 10</td>
<td>$-$</td>
</tr>
<tr>
<td>WC - 57 NbC</td>
<td>1340 ± 50</td>
<td>$-$</td>
<td>50 ± 10</td>
<td>$\sim 0.43$, $2.5 - 6$, $1 - 2$</td>
</tr>
<tr>
<td>WC - 73 NbC</td>
<td>$\sim 1350$</td>
<td>$-$</td>
<td>70 ± 10</td>
<td>$\sim 0.41$, $4 - 7$, $1.5 - 3$</td>
</tr>
<tr>
<td>NbC 0.99</td>
<td>875 ± 50</td>
<td>1750</td>
<td>190 ± 20</td>
<td>$0.28 - 0.32$, $5 - 26$, $2 - 9$</td>
</tr>
<tr>
<td>NbC 0.97</td>
<td>875 ± 50</td>
<td>1800</td>
<td>200 ± 20</td>
<td>$0.26 - 0.32$, $8 - 24$, $3.5 - 8$</td>
</tr>
<tr>
<td>NbC - 5 TaC</td>
<td>900 ± 25</td>
<td>1850</td>
<td>270 ± 20</td>
<td>$0.32 - 0.40$, $6 - 15$, $2.5 - 5.5$</td>
</tr>
<tr>
<td>NbC - 62TaC</td>
<td>875 ± 25</td>
<td>1660</td>
<td>270 ± 20</td>
<td>$0.36 - 0.46$, $5 - 14$, $2 - 5$</td>
</tr>
<tr>
<td>TaC</td>
<td>860 ± 20</td>
<td>1500</td>
<td>270 ± 20</td>
<td>$0.36 - 0.46$, $4 - 12$, $1.7 - 4$</td>
</tr>
<tr>
<td>TiC - 22 WC</td>
<td>1110 ± 50</td>
<td>2215</td>
<td>160 ± 20</td>
<td>$0.36 - 0.46$, $5 - 8$, $2 - 3$</td>
</tr>
<tr>
<td>TiC - 42 WC</td>
<td>1125 ± 75</td>
<td>2000*</td>
<td>120 ± 20</td>
<td>$0.41 - 0.43$, $3.7 - 4.7$, $1.5 - 2$</td>
</tr>
<tr>
<td>WC</td>
<td>$1200^*$</td>
<td>$\sim 1900^*$</td>
<td>$-$</td>
<td>$\sim 0.4$, $1.5 - 3$, $0.5 - 1$</td>
</tr>
</tbody>
</table>

* From reference (25)
FIGURE 54 The relationship between the hardneses of alloys with 20 vol% binder phase and the hardneses of their constituent carbides.
Thus, it is to be noted that those alloys with a high hardness relative to the carbide hardness, have a relatively high contiguity and fine grain size.

7.2.3. The Effect of Microstructural Parameters on Hardness

A quantitatively accurate, theoretical description of the influence of the microstructure on the mechanical properties of cemented carbides does not exist. Neither is it within the scope of this investigation to make a precise analysis of the problem. However, a semi-quantitative approach will be used in an attempt to relate the hardness of the alloys of this investigation to their microstructures.

Let it be supposed that the overall hardness is related to the resistance to plastic deformation of the microstructure, and is made up of separate contributions from the carbide and the binder phase. It may reasonably be proposed that the contribution of the carbide phase is related to the relative amount present, to the carbide hardness, and to the carbide contiguity. Thus:

\[ H_c^{'} = a H_c G + b H_c (1 - \alpha) \]

\( a \) and \( b \) being constants.

The contribution of the binder phase will be related to its hardness and to the relative amount present. The resistance to plastic deformation of the binder phase is probably related largely to the pile-up of dislocations at the carbide/binder interfaces, and will, therefore, depend on the mean free path in the binder phase. Thus, the contribution of the binder phase is written:

\[ H_b^{'} = (H_b + d \bar{l}^{-\frac{1}{2}}) \]

d being a constant. This equation is based on that for the effect of grain boundaries on yield in polycrystalline metals.\(^{169}\) inter al.

Combining the two contributions:

\[ H_v^{'} (\text{alloy}) = a H_c G + b H_c (1 - \alpha) + \alpha H_b + \alpha d \bar{l}^{-\frac{1}{2}} \]  

(72)

The constants, \( a \), \( b \), and \( d \) would be expected to depend on the phases.
concerned. The hardness of the undeformed binder metal, \( H_b \), would depend, not only on the properties of the pure binder metal, but also on the effects of solid solution hardening, and possibly precipitation hardening.

It was found empirically that the following approximate values for the constants gave satisfactory agreement with the alloys investigated: 
\[
a = 0.7; \quad b = 0.25; \quad d = 300; \quad \text{and} \quad H_b = 300; \quad (\bar{I} \text{ being in microns}); \quad \text{so that:}
\]

\[
H_V = H_c(0.7G + 0.25(1-\eta)) + 300 \alpha(1 + \bar{I}^{-2}) \quad (73)
\]

In Figure 55, experimental values of hardness for a number of representative specimens are shown in comparison with values predicted for them by equation (73). The equation gives good agreement with the experimental values, except for those alloys of WC-Co and NbC-Co that had large grain size and low contiguity. It is probable that a fine precipitate of the carbide in the binder phase (see section 3.1.3.) raised the effective value of \( H_b \), or reduced the effective value of \( \bar{I} \) in these specimens.

While it must be admitted that equation (73) can only be loosely related to the fundamental nature of the hardness, it does serve to illustrate the relative importance of the various microstructural parameters. Thus, for the ranges of parameters observed in the alloys of this investigation, the volume fraction of the phases and the carbide contiguity had a greater influence on the hardness than did the fineness of the microstructure. However, the mean free path of the binder phase is expected to exert a greater influence when it falls below about 1 micron. Such an effect is observed in the case of the strength of WC-Co alloys, for which the effect of \( \bar{I} \) becomes less significant as \( \bar{I} \) increases above about 1 micron (see Figure 7).

7.3. The Energy of Crack Formation of the Alloys

7.3.1 The Crack Path

In all the alloys that were tested (i.e. those included in Table 34), the path of the crack, initiated at the corners of the hardness indentation, passed mainly through the carbide phase; it sometimes followed the carbide/binder interface and, more rarely, passed
FIGURE 55 A comparison between the measured hardness of certain alloys, and values predicted by equation (73).
through the binder phase or along contiguous boundaries. A typical example of such a crack is shown in Figure 56. Frequently, the crack was discontinuous (in two dimensions), i.e. it was arrested at areas of cobalt but continued in a neighbouring grain.

Such observations are of significance in the assessment of the effect of the microstructure on the toughness of the alloys.

7.3.2. The Effect of Binder-Phase Content on the Resistance to Cracking

The effect of binder-phase content on the resistance to cracking of the alloys investigated is shown in Figure 57. In all the alloys there was an increase in crack resistance with increase in binder content. The effect became more marked in TaC-Co and TiC-Co above a binder content of about 10 vol%. This could possibly be associated with a change in the degree of continuity of either of the phases, although this would require a more detailed study in order to be confirmed.

There appeared to be little influence of the carbide grain size on the toughness, with the notable exceptions of TaC-Co and TiC-Co alloys with grain sizes of \( \delta < 5.5 \) microns. The effect of microstructural parameters will be discussed in section 7.3.4.

7.3.3. The Effect of the Carbide Phase on the Resistance to Cracking

The insensitivity of the resistance to cracking to the carbide grain size above about 5 microns makes it possible to compare the relative toughness of the alloys, for a fixed binder content, without having to allow for grain size. Such relative values of \( W \) are included in Table 34. Of the alloys investigated, those of TiC and TaC were the toughest. It is also to be noted that small additions of TaC to NbC improved its toughness without reducing its hardness, an effect already observed in commercial alloys\(^1\).

Although the alloys of this investigation are primarily of an experimental nature, it would be of interest to compare their toughness with that of commercial alloys. The only reported value of \( W \) for a commercial alloy is 70 kg/mm for a fine-grained WC-Co alloy which contained 6 wt% (about 10 vol%) cobalt and had a hardness of \( 1740 \) kg/mm\(^2\) (159). Since this alloy had a lower binder content and a much finer grain size than the alloys of this investigation, a precise comparison is not possible. It is apparent, however, that their toughness is of a similar order of magnitude.
FIGURE 56  A crack initiated at the corner of a Vickers hardness indentation (at the top right-hand corner).

(Alloy: (NbC-80mol% VC)-20vol% Co)

800 X
FIGURE 57 The effect of binder phase content on the resistance to cracking of TaC-Co and TiC-Co alloys
7.3.4. The Effect of Microstructure on Resistance to Cracking

As for the case of hardness, there is no satisfactory quantitative description of the effect of microstructural parameters on the resistance to fracture, or the toughness, of cemented carbides. Furthermore, since little is known of the relative toughness of the unalloyed carbides, it is not even possible to derive semi-empirical relationships, as was the case for hardness. However, certain qualitative effects can be predicted.

It seems generally accepted that, even when such alloys as cemented carbides fail in a brittle, catastrophic manner, the energy of fracture is made up predominantly of the work of plastic deformation, which occurs in a region close to the crack \(^{(25)}\). In cemented carbides, it is reasonable to suppose that the majority of deformation will occur in the relatively ductile binder phase, even when the crack passes through the carbide. For this reason it is to be expected that the resistance to fracture will increase with increasing binder phase content, regardless of the fracture path.

Contiguity of the carbide will be expected to have an effect which is partially independent of the binder phase content. At a fixed binder content, if the contiguity decreases, a crack passing through the carbide will be forced to become more tortuous, or to pass through the binder phase, and therefore the work of fracture will be increased.

It is probable that the binder phase areas will be deformed by a passing crack, to an extent dependent on their mean free path, such that the work of deformation will be an inverse function of the mean free path length. Very fine binder phase areas, however, might be so resistant to deformation that they take on the characteristics of a brittle material, thereby causing a maximum in the work of fracture vs. mean free path relationship, as is the case for the transverse rupture strength (section 1.1.6.1.).

Some of these predictions are supported by the behaviour of the alloys of this investigation. The effect of increasing binder phase content was clearly demonstrated. The effect of contiguity would be largely combined with that of binder content, but it is to be noted that those alloys with a low resistance to cracking had high values of \(G(\alpha = 0.2)\). The results for the TaC-Co alloys suggest that the
resistance to cracking becomes sensitive to the mean free path of the binder phase when the latter is less than about 2 microns. For values of $\bar{1}$ below this the toughness of the TaC-Co alloys increased considerably, as Figure 57 indicates. There was no evidence of a maximum in the resistance to cracking at a certain value of $\bar{1}$. However, it is probable that such a maximum would exist at values of $\bar{1}$, below those occurring in the alloys of this investigation. The maximum in the transverse rupture strength of WC-Co alloys occurred at a mean free path of about 0.5 microns (Figure 7).

7.4. Conclusions of the Investigation of the Mechanical Properties

In general, the observed effects of the microstructure on the mechanical properties of the alloys investigated, were consistent with the findings of other investigations involving commercial WC-Co and WC-TiC-Co alloys. With increasing binder phase content, the hardness was reduced and the toughness, measured in terms of resistance to cracking, was increased. It has also been demonstrated that an increase in the carbide contiguity results in an increase in hardness. The coarseness of the microstructures did not appear to affect significantly the hardness of a given alloy for values of the mean free path of the binder phase above about 1 micron. Similarly, the toughness was not affected significantly for values above about 2 microns. For values of $\bar{1}$ below these, the hardness and toughness increased. The investigation probably did not cover a sufficient range of microstructures to detect a maximum in the toughness at a certain value of $\bar{1}$, as has been observed for the transverse rupture strength.
CHAPTER 8

GENERAL CONCLUSIONS

The following conclusions may be drawn from the results of this work.

During liquid-phase sintering, the carbide grains in cemented carbides grow predominantly by processes of solution and recrystallization, and the principles of the coalescence hypothesis are not applicable to these alloys (section 4.2.1.).

In alloys of VC-Co and Mo\textsubscript{2}C-Co, the growth is controlled by diffusion of the carbide atoms through the liquid phase. In the alloys of TiC-Co, HfC-Co, NbC-Co, and TaC-Co, another rate-controlling mechanism is involved, although for NbC-Co the mechanism is probably in transition from this to diffusion control. The growth behaviour of these single carbide alloys can be related to the thermodynamic stability of the carbide, but the growth in WC-Co alloys is atypical in this respect and it is suspected that the mechanism of rate control is unusual in this system. (section 4.2.3.).

In alloys containing two carbides, the composition of the carbide phase is shifted, with respect to the overall composition, towards the constituent carbide with the lower solubility in the binder phase (sec.3.3). Correspondingly, the ratio of the carbides dissolved in the binder phase is shifted in the other direction. For this reason, and also because new rate-controlling mechanisms can be introduced, the grain growth of a carbide is usually inhibited when another carbide is added. When more than one carbide phase is present in the microstructure, the growth almost ceases, because of locking by immobile interphase boundaries (section 4.2.3.3.).

During sintering, the (100) faces of the grains of the cubic monocarbides tend to develop, and so produce a cubic grain shape with various degrees of rounding of the cube edges. It has been shown that the degree of rounding is very sensitive to the degree of anisotropy of the interfacial energy between the carbide and the binder phase (Ch.5).

During sintering, contiguous boundaries form between the carbide grains. As sintering proceeds, the contiguity develops towards a constant value, which is an equilibrium value directly related to the wettability in the microstructure, i.e. to the relative values of the
carbide/binder-phase interfacial energy and the contiguous-boundary energy, but not to the wettability measured by the sessile-drop test (section 6.4.).

The extent to which the contiguity decreases or increases during sintering depends on the relative values of the equilibrium contiguity and the contiguity at the start of sintering. The value at the start of sintering depends on the extent of the solid-state sintering of the carbide that occurs during heating-up or during pre-sintering treatments. (section 6.2.1.).

In the majority of cemented carbides, the carbide phase is apparently in the form of a continuous skeleton during sintering (section 6.5.).

Most of the alloys that were investigated exhibited very rapid and efficient densification, regardless of the contiguity and continuity of the carbide (section 3.1.1.; Table 15). The densification is considered to occur mainly by a re-arrangement process with a solution-reprecipitation process occurring simultaneously. A model of shrinkage has been proposed which shows qualitatively that this need not necessarily be inconsistent with the existence of an apparently continuous carbide skeleton (section 6.6.).

It is concluded that the main condition favouring efficient densification is a combination of a high liquid surface energy and a low angle of contact of the liquid on the solid. A high solubility of the carbide in the liquid and a high rate of transport through the liquid also favour densification, although the latter is apparently not essential (section 3.1.1.).

The hardness and the resistance to cracking of the alloys that were studied are very sensitive to the binder-phase content, but not very sensitive to the mean free path, $\bar{I}$, of the binder phase for values of $\bar{I}$ above about 2 microns. The hardness, at a fixed binder content, increases with increasing contiguity. The variations in contiguity, normally observed in individual alloys, however, are seldom sufficient to produce a measurable change in hardness. (Chapter 7).

Suggestions for Further Work

In the majority of cemented carbide alloys the precise mechanism of control in the grain-growth process has not been revealed. In particular, the relative importance of interfacial-reaction control and contiguous-boundary control require further investigation. In this respect it
would be of value to study:

a) the dissolution kinetics of the carbides in liquid cobalt and similar metals;

b) the growth of carbide particles in high volume fractions of liquid, such that there would be little contact between the particles;

c) the grain growth of the carbides alone.

Ideally, a study should be made of the growth behaviour of the carbides as a function of the volume fraction of the liquid phase in a range between very high and very low fractions.

In combination with the studies of grain contact, the observations of the shrinkage behaviour of the investigated alloys, though limited, were sufficient to indicate that a re-appraisal of the existing models of densification are necessary. Simultaneous studies of densification and grain contact at all stages of sintering would be very beneficial. Since the major proportion of shrinkage occurs very rapidly, such a study would probably require the development of more sophisticated experimental techniques than have hitherto been used. To aid the formulation of a generalised theoretical model of densification, covering a wide variety of systems, it would be desirable to study a wide range of alloys, attention being paid to the relative roles of wettability, solubility and material transport.

An interesting study of the anisotropy in cubic carbides could probably be made on the basis of the quantitative measurement of grain shape introduced in this work. The investigation could be combined with microhardness measurements, which have already been used to study the anisotropy of carbides.

The precise influence of the microstructure on the mechanical properties of cemented carbides is still not well-understood. Attempts should be made to separate the relative contributions of the different microstructural parameters and to determine the roles of the constituent phases. This might be achieved by the exhaustive study of a very wide range of alloys. It would be more satisfactory, however, if by careful control of the microstructure of selected alloys, a single parameter such as contiguity could be varied without causing large changes in other parameters. This could perhaps be achieved by use of a variety of methods of specimen manufacture.
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APPENDIX 1

Symbols used frequently in the text

- \( a \) Edge length of a cube.
- \( A \) Area of a particle surface.
- \( \alpha \) Volume fraction of the binder phase.
- \( C_o \) Equilibrium solubility of the carbide in the liquid binder phase, at a plane interface.
- \( C_r \) Solubility of the carbide in the liquid binder phase at an interface of radius \( r \).
- \( \bar{C}_r \) Solubility of the carbide in the liquid binder phase in a dispersion of particles with average radius \( \bar{r} \).
- \( \bar{d} \) Mean intercept length of carbide grains at time \( t \).
- \( d_0 \) Mean intercept length of carbide grains at the start of sintering.
- \( d_m \) The mean intercept length of the largest grain in a microsection.
- \( D \) Coefficient of diffusion.
- \( F_A \) Grain shape parameter.
- \( G \) Contiguity of the carbide grains.
- \( \gamma_{lv} \) Surface energy of a liquid.
- \( \gamma_{sl} \) Interfacial energy between the carbide and the binder phase.
- \( \gamma_{ss} \) Energy of the carbide grain boundary.
- \( \gamma_{sv} \) Surface energy of a solid.
- \( H_v \) Vickers hardness number.
- \( \Delta H \) Heat of Formation.
- \( k_r \) Rate constant of an interfacial reaction.
- \( K_D \) Grain growth rate constant for growth controlled by diffusion through the binder phase, expressed in terms of \( \bar{r} \).
- \( K_d \) Grain growth rate constant for growth controlled by diffusion through the binder phase, expressed in terms of \( \bar{d} \).
Grain growth rate constant for growth controlled by an interface reaction, expressed in terms of $\bar{r}$.

Grain growth rate constant for growth controlled by an interface reaction, expressed in terms of $\bar{d}$.

Growth rate constant for solid state grain growth.

Mean free path in the binder phase.

Total length of cracks emerging from a hardness indentation.

The binder phase metal.

The transition metal constituent of a carbide.

The exponent in grain growth equations.

The average number of inter-particle contacts per particle.

Number of features per unit area of a microsection.

Number of features per unit volume of a specimen.

Number of carbide/binder phase interfaces intersected by a random intercept line.

Number of contiguous boundaries intersected by a random intercept line.

Activation constant for carbide grain growth.

Dihedral angle.

Grain boundary groove angle.

Particle radius.

Mean particle radius of a group of particles.

Radius of the largest particle in a group of particles.

Effective radius of a non-spherical particle.

Universal gas constant.

Interfacial area.

Temperature.

Eutectic temperature.

Angle of contact of a liquid on a solid.
The time taken to reach a steady-state particle-size distribution during the growth of particles dispersed in a liquid.

\( V \) Volume, usually of a particle.

\( W \) The resistance to cracking, \( = \frac{P_h}{L_0} \) where \( P_h \) is the load in a Vickers hardness test.

\( \Omega \) Molar volume.