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Microstructural development during the liquid-phase sintering of VC-Co alloys

R. WARREN
Department of Metallurgy and Materials Technology, University of Surrey, Guildford, Surrey, UK

A study was made of the microstructural changes that occur during the liquid-phase sintering of VC-Co alloys. It was found that considerable growth of the carbide grains takes place and that this growth can be described by the equation:

$$\bar{d}^3 - \bar{d}_0{}^3 = Kt$$

The value of the rate constant, K, at 1450° C was found to be in good agreement with that predicted by a modified Wagner analysis for a solution/precipitation process controlled by diffusion through the liquid. The observed variations in the growth rate both with temperature, between 1380 and 1500° C, and with the volume fraction of the liquid phase are also consistent with this theory.

The contiguity of the carbide grains at the start of sintering is relatively high and is affected by the pre-sintering history of the specimen. During the early stages of sintering, however, the contiguity falls rapidly to a low value which subsequently remains relatively constant. Observations were made which suggest that the carbide does not form a continuous skeleton during sintering.

1. Introduction

Liquid phase sintering is a powder-metallurgical process in which a small proportion of the material being sintered is in the liquid state. Materials produced by this technique generally consist of particles or grains of one or more phases dispersed in a binder phase, which during sintering is the liquid phase. Knowledge of the microstructural changes that occur during liquid-phase sintering is of importance because of the influence of the microstructure on many of the properties of materials produced by this technique and also because it can lead to a better understanding of the mechanisms of the sintering. Studies of the way that the microstructure develops during the sintering have been made on a large range of materials including, mixed oxide systems [1, 2], heavy metal alloys [3, 4], and cemented carbides [5-11]. In spite of the wide differences in these materials, the studies have revealed a marked similarity in their microstructural development and the factors that control it.

In the present work cemented carbide alloys of VC, with cobalt as the binder phase, have been investigated in the light of the observations and conclusions of the previous studies. These earlier studies will be discussed briefly below with reference to cemented carbides.

2. Theoretical and experimental background

2.1. The growth of the carbide grains

During liquid-phase sintering, the grains of the dispersed solid phase coarsen, and it is now generally recognized that this occurs principally by a process of solution and reprecipitation. The driving force for the process results from the consequent reduction in total interfacial energy. Such a process has been analysed theoretically, for the case of spherical particles and small volume fractions of solid phase, by, among others, Wagner [12]. For growth, controlled by diffusion of the solid phase atoms through the liquid, Wagner's theory leads to the isothermal growth equation:

$$\bar{r}^3 - \bar{r}_0{}^3 = K_\mathrm{D}t \qquad (1)$$

where $\bar{r}$ is the mean particle radius at time t, $\bar{r}_0$ is the initial mean particle radius, and K_D is a temperature-dependent constant such that:

$$K_\mathrm{D} = \frac{8\gamma_\mathrm{SL}\Omega^2}{9RT}\, D\, C_0$$

where γ_{SL} is the energy of the solid-liquid interface per unit area, Ω is the molar volume of the solid, D is the coefficient of diffusion of atoms of the solid in the liquid, C_0 is the solubility of the solid in the liquid, R is the gas constant and T the absolute temperature.

For growth controlled by a reaction at the solid-liquid interface, Wagner's derivation leads to the equation:

$$\bar{r}^2 - \bar{r}_0^2 = K_R t \tag{2}$$

where the constant

$$K_R = \frac{64\gamma_{SL}\Omega^2}{81\ RT}\, k_r\, C_0$$

and k_r is the rate constant for the interfacial reaction.

The derivation of Equation 1 was based on the assumption that the effective diffusion path length through the liquid is related to the particle radius. However, when the volume fraction of the solid phase is large, as is the case in liquid-phase sintering, the diffusion path length is related to the distance between the particles and consequently, the rate of diffusion-controlled growth is expected to be affected by the volume fraction of the phases. To allow for this effect, the Wagner analysis was modified by Sarian and Weart [7] and by Lay [2]. For example, Sarian and Weart assumed that the effective diffusion path length is related to the mean free path through the liquid and thereby obtained the equation:

$$\bar{r}^3 - \bar{r}_0^3 = \frac{4}{3} \cdot \frac{1-\beta}{\beta} \cdot K_D t \tag{3}$$

where β is the volume fraction of the liquid phase. A very similar equation was obtained by Lay. In a very recent and more rigorous modification of the Wagner analysis, Ardell has shown that the growth rate is affected even at low volume fractions of the solid phase [13].

An important assumption in the above derivations is that the dispersed grains are not in contact. However, many investigations have shown that, during liquid-phase sintering, the grains of the solid phase form contiguous boundaries. Such contact could be expected, in certain circumstances, to modify the grain growth, either as a physical barrier to the advance of the solid-liquid interface [1, 8], or by modification of the curvature of the interface [1]. In the former case, the contiguous boundary can be thought of as acting as a drag on the solid-liquid interface and it is conceivable that the movement of such boundaries could become the rate-controlling step in the growth process. A quantitative, theoretical description of growth controlled in this way has yet to be formulated.

If, in certain systems, control by diffusion through the liquid is retained in spite of particle contact, then the degree of contact might still be expected to influence the growth rate via its geometric effect on the diffusion path length. Thus it can be shown that the mean free path through the liquid phase is given by:

$$l = \frac{4}{3} \cdot \bar{r} \cdot \frac{\beta}{1-\beta} \cdot \frac{1}{1-G}$$

where G is the contiguity, defined as the average fraction of the surface area of a grain of the solid phase shared with all neighbouring grains [5]. If this value of l is used in a derivation analogous to that of Sarian and Weart, then the following equation for diffusion-controlled growth is obtained:

$$\bar{r}^3 - \bar{r}_0^3 = \frac{9}{8}(1-G)\frac{(1-\beta)}{\beta} \cdot K_D t \tag{4}$$

The theories discussed above suggest the following means for the interpretation of the growth behaviour of real systems observed experimentally, and in particular for distinguishing between interface reaction and diffusion controlled growth:

(i) The comparison of experimental with theoretical growth rate constants and the comparison of their temperature dependence: this method is limited by the availability of data for substitution into the theoretical constants [9].

(ii) The determination of the experimental exponent, n, in an equation of the form $\bar{r}^n - \bar{r}_0^n = Kt$: However, the ability to distinguish accurately between a value of $n = 2$ and $n = 3$ is limited by experimental accuracy, and the distinction becomes increasingly uncertain with decreasing growth rates [10].

(iii) The determination of the effect of the volume fraction of liquid phase on the growth rate: The diffusion-controlled growth rate should be dependent on β whereas the reaction-controlled growth rate should be independent of β.

(iv) The measurement of the grain size distribution [10, 14]: Wagner predicted different steady-state size distributions for the two mechanisms of control. Thus the value of $r_{max}/\bar{r}$ for diffusion-controlled growth was predicted as 1.5 and for reaction-controlled growth as 2.25. Ardell has predicted, however, that, at high volume fractions of solid, the distribution for diffusion-control becomes very similar to that for reaction-control, and that for the volume fractions present in liquid-phase sintering the value of $r_{\max}/\bar{r}$ for diffusion-control is also close to 2.25 [13]. Even if the distributions are distinguishable, the method is hampered by the extreme difficulty or impossibility of measuring the distributions for non-spherical particles with sufficient accuracy.

Investigations of a variety of cemented carbide systems have often revealed only partial agreement with one particular growth mechanism. The grain growth of NbC in liquid cobalt, nickel and iron exhibited values of growth rate constant and exponent, n, in good agreement with the theoretical values for diffusion-controlled growth [7-9]. However, the variation of growth rate with temperature in these systems gave values of "activation energy" which seem too high to be accounted for only by changes in C_0 and D, which are the most thermally sensitive components of the rate constant. Furthermore, in the NbC-Fe system, the growth was not significantly affected by changes in the liquid content [7].

In a study of VC-Co and VC-Ni alloys, Exner *et al* measured "activation energies" which were low enough to be consistent with diffusion-controlled growth, but on the basis of the measurement of the grain-size distributions, it was concluded that the growth was controlled by an interfacial reaction [10]. In WC-Co and (W,Ti)C-Co alloys, the carbide growth rates are so low and the "activation energies" so high, that it is almost certain that the growth is not diffusion-controlled [6, 11].

The apparent failure of the experimental growth behaviour of some systems to conform completely to any one theoretical growth mechanism might be due to limitations in the experimental techniques available for such studies. It is also possible, however, that the growth deviates from that of the ideal theoretical models as a result of, for example, grain contact or non-spherical grain shape.

2.2. Contact between carbide grains

Stephenson and White have demonstrated theoretically that, at a given ratio of the solid-liquid interfacial energy and the solid-grain boundary energy, an array of particles would be expected to attain an equilibrium degree of contact having a minimum total energy [1]. In support of this, the movement towards a constant degree of contact during liquid-phase sintering has been observed in a variety of systems, by measurement of the contiguity [5, 6, 8]. There remains, however, some uncertainty with regard to the degree of contact at the *beginning* of sintering. The study of WC-Co and TiC-Co alloys by Gurland suggested that the contiguity was initially very low and *increased* during sintering [5], whereas Exner and Fischmeister [6] and Warren [8] observed the opposite, i.e. a *fall* in contiguity, in alloys of WC-Co and NbC-Co respectively. Nevertheless, it is significant that the contiguity was, after prolonged sintering, similar in both the studies of the WC-Co alloys.

A second important aspect of grain contact is the continuity of the solid phase, i.e. the degree of "interconnectedness" of the solid-phase grains. Gurland has shown that this property can be measured in terms of the number of contiguous contacts per grain [15-17]. He demonstrated both experimentally and theoretically that at a critical value of approximately 1.5 contacts per grain, there is a transition between a discontinuous and a completely continuous grain structure [16, 17]. The question of whether or not the carbide phases in cemented carbides exist as continuous skeletons has long been a matter of controversy. This is partly due to the difficulty in the direct measurement of continuity. The number of contacts per grain, can be measured by quantitative metallography, but the method is accurate only if the grains are uniformly-sized spheres with uniformly-sized areas of contact [17].

Because grain contact is partly dependent on the statistical probability of the spatial coincidence of the grains, contiguity and continuity are expected to be a function of the volume fraction of the phases. This has been demonstrated experimentally in a number of investigations [5, 6, 16].

2.3. The shape of the carbide grains

Investigations of a large number of cemented carbide systems have shown that, during liquid-phase sintering, the carbide grains develop characteristic shapes which are recognizable even though distorted by grain impingement and contact. In WC-Co alloys the shape is a triangular prism [18] and in alloys of the cubic carbides the shape ranges from cubic, with various degrees of rounding of the edges and corners, to near-spherical [19-21]. The shape of the carbide grains in VC-Co and VC-Ni alloys has already been found to be very nearly spherical [10, 21].

3. Experimental details

3.1. Materials and preparation of alloys

Alloys of VC with cobalt were prepared from high-purity carbide and cobalt powders. The oxygen content of the carbide was approximately 0.05 wt %. The carbide in the alloys was made up of a mixture of two powders containing 18.4 and 17.2 wt % carbon respectively. The mixture was adjusted to give a carbon content of 17.4 wt %, corresponding to a formula $VC_{0.91}$. This was found, by test-sintering, to be the highest carbon content which did not give free carbon in the sintered microstructure.

The mean particle size of the carbide powder was 5 μm and of the cobalt 1.4 μm.

Alloys were prepared with between 5 and 20 vol % cobalt. The alloy powders were mixed for 24 h in rotating polythene bottles. Acetone was used as a mixing medium in order to enhance the mixing process and to minimize oxidation of the powders. Just before sintering, the mixed powders were pressed into cylindrical specimens, 1 cm in diameter and approximately 1 cm high, using a pressure of 4000 kg/cm^2.

3.2. Sintering

The specimens were sintered on a substrate of VC chips in a molybdenum-wound resistance furnace in a vacuum of $\sim 10^{-5}$ torr. Except in an investigation of the effect of pre-sintering treatments, they were heated from room-temperature to about 1250°C in approximately 2 h. Heating from 1250°C, which is below the temperature of liquid formation, up to the sintering temperature was carried out as quickly as possible and took between 1 and 2 min depending on the sintering temperature. The sintering time was measured from the instant that the sintering temperature was reached. The sintering temperature was measurable to ± 5°C using a thermocouple placed just above the specimen, and was controlled to within $\pm$ 1°C of the set temperature. After sintering, the specimens were allowed to furnace-cool, their temperature falling well below the melting point of the binder phase within 60 sec. Analysis of sintered specimens revealed no loss in the carbon content of the carbide.

3.3. Metallography

The specimens were sectioned with diamond grinding wheels and polished with diamond paste on polishing wheels. The microstructures were revealed satisfactorily by etching in a boiling solution of 20 % potassium ferricyanide and 20 % potassium hydroxide.

All quantitative metallographic measurements were made on suitably enlarged optical micrographs. The volume fraction of the phases was determined by point counting with a regular grid of points.

The carbide grain size was measured in terms of the mean intercept length, which is given by:

$$\bar{d} = \frac{L(1 - \alpha)}{N}$$

N being the number of grains intersected by random straight lines, of total length L, drawn through the microstructure and α being the volume fraction of the binder phase at room temperature. At least 500 grains per specimen were counted. The contiguity of the carbide was measured by counting the intersections of random test-lines with the carbide-binder interfaces and the contiguous boundaries. On certain specimens, measurement was also made of the number of contacts per grain using the method of Gurland [17].

3.4. The measurement of solubility, C_0 and interfacial energy, γ_{SL}

To determine the value of the theoretical grain-growth rate constant for comparison with the experimentally observed value, it was necessary to obtain a value of the solubility of the carbide in liquid cobalt and the value of the interfacial energy between the carbide and the liquid phase.

The measurement of the interfacial energy was accomplished by use of the method of multiphase equilibrium and has already been described [22]. An approximate value for the solubility of VC in liquid cobalt at 1450°C was determined by melting a small amount of high purity cobalt in contact with a polycrystalline specimen of VC in an alumina crucible. After cooling, the cobalt drop was sectioned and analysed for vanadium using electron probe micro-analysis.

4. Results and discussion

4.1. General observations

All the specimens exhibited very rapid densification, reaching a density of 99.9 % of the

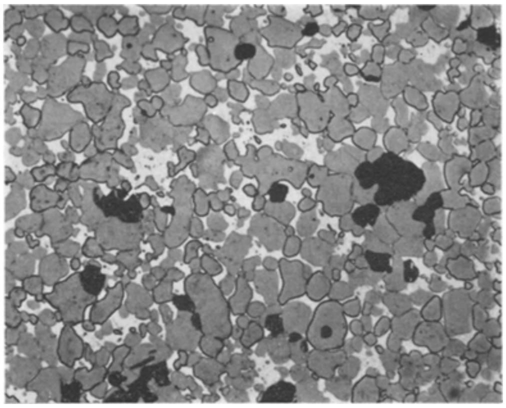

Figure 1 Microstructure of the alloy VC-20 vol % Co at the start of sintering; $T = 1380°C$, $t = 0$ min (× 280).

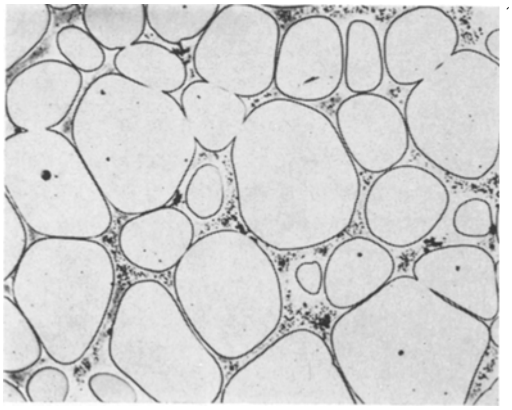

Figure 2 Microstructure of the alloy VC-20 vol % Co sintered at 1380° C for 120 min (× 280).

theoretical within the first few minutes of sintering. They did not retain a perfectly cylindrical shape but tended to "flow" during sintering. The implications of this are discussed in Section 4.3

Typical microstructures of specimens at the start of sintering and after 2 h of sintering are shown in Figs. 1 and 2. These illustrate the main features of the microstructural development that occurred during sintering, namely, marked grain growth, a decrease in grain contact, a narrowing of the grain size distribution, and a change from an irregular grain shape to a rounded, near-spherical shape.

4.2. Carbide grain growth

The growth of the carbide grains was very pronounced and, as shown in Fig. 3, fitted very closely to an equation of the form $\bar{d}^3 - \bar{d}_0^3 = Kt$, where $\bar{d}$ is the mean linear intercept of the carbide grains. Values for the growth rate constants could therefore be obtained by measuring the slope of the plots of $\bar{d}^3$ versus t. It was found that agreement of the results with the equation $\bar{d}^2 - \bar{d}_0^2 = Kt$ was far less satisfactory.

The effect of temperature on the growth rate is illustrated in Fig. 4 as an Arrhenius plot. The growth rates measured at the three temperatures above the melting point of the liquid phase give an "activation energy", Q, of 33 ± 7 kcal/mol. This is in fair agreement with the value of 26 kcal/mol determined by Exner *et al*, and is consistent with the expected effect of temperature on diffusion-controlled growth.

The melting point of the liquid phase, i.e. the

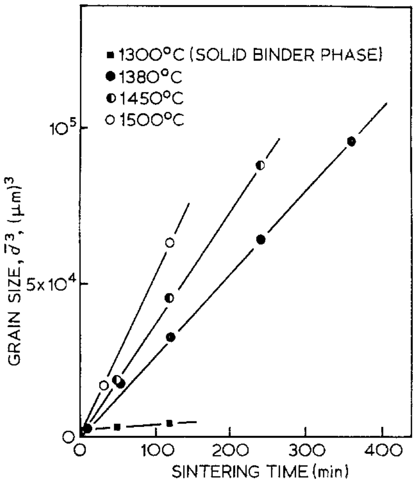

Figure 3 Grain growth of VC in the alloy VC-20 vol % Co, plotted as $\bar{d}^3$ versus t.

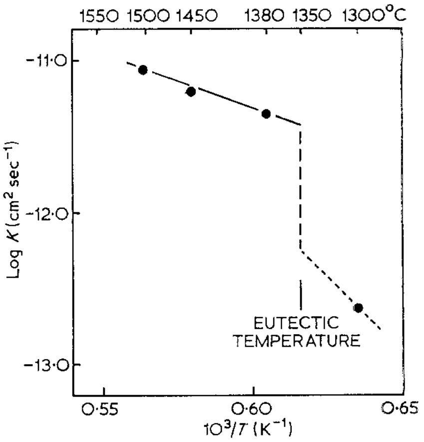

Figure 4 Effect of temperature on the grain growth of VC in the alloy VC-20 vol % Co.

TABLE I Comparison of theoretical and experimental grain-growth rate constants for VC in Co at 1450° C

Interfacial energy γ_{SL} (ergs/cm^2)	Solubility C_0 (mol/cc)	Growth rate constants* (cm^3/sec) × 10^{12}		
		Equation 1	Equation 4	Experimental
464 ± 120	2.1 × 10^{-2}	1.45	4.13	6.02

*The constants are given in terms of $\bar{d}$ rather than $\bar{r}$. For spherical particles $\bar{d} = \frac{4\bar{r}}{3}$ and therefore $K_D(\bar{d}) = \frac{64}{27} K_D(\bar{r})$.

eutectic temperature of the VC-Co system, is known to be approximately 1350° C [23]. The carbide growth rate was determined just below this by annealing at 1300° C a specimen that had previously been sintered to full density at 1380° C. This served to demonstrate the marked effect of the presence of the liquid on the growth, as is also shown in Fig. 4.

Comparison of the experimental growth rate constant at 1450° C with the theoretically-predicted values of Equations 1 and 4 is made in Table I, which also includes the values of C_0 and γ_{SL} determined in this investigation. The coefficient of diffusion, D, for VC in liquid cobalt was taken as 5×10^{-5} cm^2/sec for the purposes of the calculation of the theoretical constants. Very little information exists on the diffusion in such systems and the assumed value was based on existing data for the diffusion of carbon and certain transition metals in liquid iron. In view of this and because of the difficulty of defining the diffusion in a system containing a compound [24], this value can be considered correct only to within an order of magnitude. Taking account of this uncertainty, the agreement between the theoretical and experimental growth constants is very good.

The effect of the volume fraction of the binder phase (measured by quantitative metallography on the sintered specimens) on the carbide growth rate at 1450° C is shown in Fig. 5. There was a marked increase in growth with decrease in binder content. The observed effect is in very good agreement with that predicted by Equation 4, shown as the dotted curve in Fig. 5. In the calculation of this curve allowance was made for the increase in volume fraction of the binder due to the higher solubility of the carbide at the sintering temperature. Because of the low degree of contact of the carbide grains in this system, agreement of the experimental results with Equation 3 is also very satisfactory.

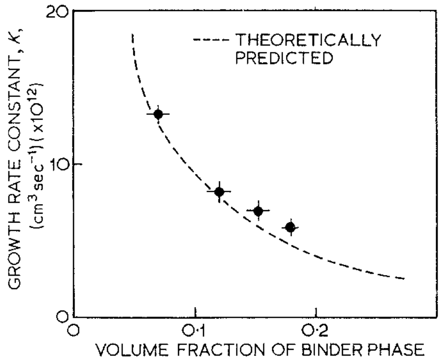

Figure 5 Effect of binder phase content on the grain growth of VC in VC-Co alloys; dotted line shows effect predicted by Equation 4.

Although the carbide grains could be described as near spherical, it was considered that they were too distorted by impingement to permit an accurate analysis of the grain-size distribution. Instead an estimate was made of $d_{max}/\bar{d}$, by measurement of the largest-sectioned grain in the microsections of the specimens. This value was almost certainly an underestimate since the statistical chance of finding in one microsection a particle section with the true maximum size is very slight. It was found that, for all sintering temperatures, the measured value of $d_{max}/\bar{d}$ fell rapidly from a value of about 2.8 at the start of sintering to a fairly constant value between 1.6 and 1.8 at sintering times greater than 5 min. This does suggest the existence of a stable size distribution but in view of the conclusions of Ardell, mentioned in Section 2.1, and because of the uncertainty of the measurement, the values of $d_{max}/\bar{d}$ cannot be taken as a conclusive indication of the growth control mechanism.

Nevertheless, it may be stated in conclusion that in almost every respect the carbide grain-growth behaviour in the VC-Co system is consistent with the theoretical predictions for growth by solution and reprecipitation, controlled by diffusion through the liquid phase.

TABLE II The effect of sintering conditions on the contiguity of VC-20 vol % Co alloys

Sintering temperature (°C)	Contiguity, G ($\alpha = 0.2$) at sintering times*							
	0	5	10	30	48	55	120	240 (min)
1380	0.34	—	0.15	—	—	0.14	0.13	0.10
1450	—	0.14	—	0.13	0.13	—	0.12	0.10
1500	—	—	—	0.13	—	—	0.06	—

*The contiguity values are ± 0.02.

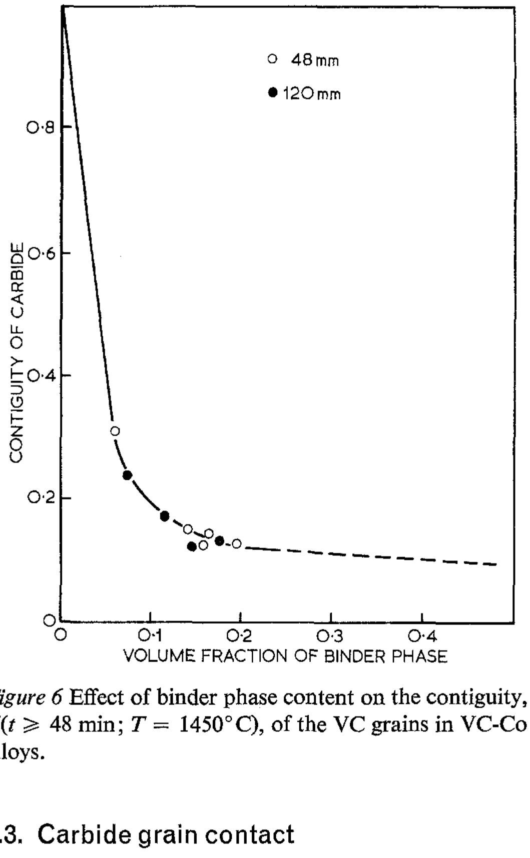

Figure 6 Effect of binder phase content on the contiguity, $G(t \geqslant 48$ min; $T = 1450°$C), of the VC grains in VC-Co alloys.

4.3. Carbide grain contact

The effect of α, the volume fraction of the binder phase on G, the contiguity of the VC grains, is shown in Fig. 6. It is to be noted that the expected decrease in G, with increase in α, is very sharp below a volume fraction of about 0.1, and less pronounced above this.

The effect of sintering on the contiguity was investigated for the alloys with a nominal composition of 20 vol % cobalt. Because of evaporation during sintering, the binder phase content was usually slightly less than this and also varied from specimen to specimen. To make direct comparison of the measured contiguities valid, therefore, their values were all adjusted to values at $\alpha = 0.2$ by applying G versus α relationships similar to that of Fig. 6. The effects of sintering time and temperature on the contiguity, $G(\alpha = 0.2)$, are summarized in Table II. The contiguity fell very rapidly from a relatively high degree of contact at the start of sintering, towards a low constant value as sintering progressed. This is consistent with the concept of an equilibrium value of contact, governed by the ratio of the interfacial energy, γ_{SL}, and the contiguous boundary energy, γ_{SS}, and discussed in Section 2.2. That this ratio is indeed low in this system is indicated by the low dihedral angle, namely $\phi = 8°$ at 1450°C [22].

The effect of the duration of heating on G_0 (the contiguity at the start of sintering) was investigated by pre-sintering specimens for different times and then heating them to the normal sintering temperature (1380°C). The results are summarized in Table III and show that the initial degree of contact is sensitive to the amount of pre-sintering. It may be concluded that the value of G_0 is determined largely by the contacts that form during the solid-state sintering that occurs during heating and is consequently dependent on the relative values of the carbide surface energy, γ_{SV}, and the boundary energy, γ_{SS}. The changes that occur in contiguity during sintering may therefore be attributed to the replacement of such contacts by a different set of contacts, determined by the relative values of γ_{SL} and γ_{SS}. The way that the contiguity changes, i.e. the extent to which it increases or decreases, during sintering will depend, therefore, not only on the equilibrium degree of contact, but also on the pre-sintering history of the compact.

All the alloys studied exhibited a very low continuity of the carbide phase. Measurements on specimens of the alloy containing 20 vol % cobalt, yielded values of approximately 2 contacts per grain, which is very close to the

TABLE III The effect of pre-sintering treatment on G_0, the contiguity at the start of sintering

Time at 1200° C (min)	Time spent above 1000° C (min)	Total heating time (min)	Contiguity $G_0(\alpha = 0.2)$
0	4	25	0.27
~5	20	105*	0.34
120	130	225	0.35
240	260	430	0.35

*The standard heating procedure.

critical value of 1.5 for the continuous-discontinuous transition for spherical particles. That the carbide did not form a continuous skeleton is indicated by the fact that the specimens tended to "flow" during sintering, since such a phenomenon would require considerable relative movement of the grains. These observations are significant since they imply that in most other cemented carbide alloys, which retain their pressed shape during sintering, and exhibit a higher degree of contact, the carbide phase *is* in the form of a continuous skeleton during sintering.

4.4. The carbide grain shape

At the start of sintering the grain shape of the VC was irregular (Fig. 1) and was presumably inherited from the original powder. After only a few minutes of sintering, however, the shape became much more regular and rounded. Unlike the shape of other carbides, it showed little evidence of anisotropy and could be described as near spherical [21]. However, as can be seen in Fig. 2, the spherical shape was distorted by impingement of the grains. Such distortion was inevitable if full densification was to occur, since the amount of binder phase in the alloys was insufficient to fill the free space between spheres, even if perfectly close-packed.

5. Conclusions

During the liquid-phase sintering of VC-Co alloys, the growth behaviour of the carbide grains is consistent, in almost every respect, with a growth process which involves solution and reprecipitation and which is controlled by diffusion through the liquid phase. Thus the growth can be described by the equation:

$$\bar{d}^3 - \bar{d}_0^3 = Kt$$

in which the experimental rate constant, K, is in good agreement with the theoretical value for such a process. The observed effect of temperature on the growth rate is reasonably consistent with theoretical expectation, having an effective "activation energy" of 33 ± 7 kcal/mol between 1380 and 1500° C. Moreover, the growth rate increases with decreasing volume fraction of the liquid phase, in a manner predicted theoretically. The ideal growth behaviour of this system can possibly be attributed to the near spherical shape of the grains and to the low degree of contact between them.

The contiguity of the carbide phase attains a relatively constant value (~0.1 for 20 vol % binder phase) after a few minutes of sintering. This is consistent with the concept of an equilibrium degree of contact, governed by the relative values of the solid-liquid interfacial energy and the contiguous boundary energy. In contrast, the contiguity at the start of liquid-phase sintering depends on the amount of solid-state sintering that occurs during heating and therefore on the pre-sintering history of the specimen. Experimental evidence suggests that the carbide phase does not form a continuous skeleton during sintering.

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