

Microstructural Development During the Liquid-Phase Sintering of Two-Phase Alloys, with Special Reference to the NbC/Co System

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Received 26 February 1968, and in revised form 18 April

An investigation was made of the grain growth and other microstructural changes occurring during the liquid-phase sintering of NbC alloys with ~20 wt % cobalt. The effects of sintering time, sintering temperature, and small alloying additions were studied. It was found that the grain growth of NbC in liquid cobalt, at 1420° C, can be described by the equation:

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

where \bar{d} is the mean linear intercept of the grains after time t , and \bar{d}_0 the initial mean intercept, K being a temperature-dependent constant with an "activation energy" of 95 ± 15 kcal/mole. This equation suggests that grain growth occurs by a solution/precipitation process controlled by diffusion in the liquid phase. Small alloying additions of WC, TiC or NbB₂ inhibit the growth and/or alter the growth process, as well as affecting such properties as the shape and contiguity of the carbide grains.

The relative significance of grain coalescence to grain growth in a liquid phase is discussed.

By examining theoretically the effect of anisotropy of interface energy on the cube \rightleftharpoons sphere grain-shape change, it has been possible to explain the observed sensitivity of grain shape towards sintering conditions.

1. Introduction

Liquid-phase sintering is a powder metallurgical process in which a small proportion of the compact being sintered is in the liquid state. One example of its application is the sintering of the class of alloys known as cemented carbides, which consist of grains of hard metallic carbides dispersed in a relatively ductile "binder" metal such as cobalt or nickel. During sintering, the binder metal together with a small amount of dissolved carbide forms the liquid phase*. Liquid-phase sintering often leads to practically

complete densification and is therefore of considerable technical interest.

It is well established that the microstructure of liquid-phase sintered alloys has a profound influence on their mechanical properties, particularly in the case of cemented carbides [1-3]. The effects of sintering conditions on microstructure are, therefore, of practical as well as theoretical interest.

Experimental studies have already been carried out on a number of systems by various investigators, particularly with regard to the grain

*When an alloy cools after liquid-phase sintering, a certain amount of the solid-phase constituent precipitates from the liquid and the microstructure developed during sintering is consequently modified. In this work therefore, the terms "binder phase" and "dispersed phase" – as distinct from "liquid" and "solid" – are used when reference is made to the fully solidified microstructure. Nevertheless, for many alloys (including the cemented carbides) the precipitation during cooling is relatively slight and the microstructure observed is probably a good indication of the state of the alloy just before cooling.

growth of the solid phase. A theoretical basis for such investigations has been the theories of particle growth in a liquid matrix, developed, by among others, Wagner [4]. In practice, however, the conditions during liquid-phase sintering often differ in a number of respects from those of the theoretical model and a comprehensive, quantitative understanding of the mechanisms of microstructural development has not been possible.

The present investigation involved the study of the influence of sintering time, sintering temperature, and minor alloying additions on the microstructural parameters: grain size, grain shape, and contiguity of the dispersed phase and also the volume-fraction and mean free path of the binder phase. The *contiguity* of a phase is defined as the average fraction of the surface area shared by one grain of the phase with all neighbouring grains of the same phase. The *mean free path* of the binder phase, in the present context, is defined as the mean, uninterrupted intercept length of the binder phase areas (not grains) measured in a random direction.

The alloys studied experimentally were of NbC with close to 20 wt % cobalt as the binder phase. The results are discussed with reference to the results and conclusions of other investigators, with the intention of gaining an understanding of the different physical and chemical factors involved as well as the relative importance of these factors.

The NbC/Co system was chosen for the investigation, partly because it was found to be particularly convenient for metallographic study, and partly because it typifies the systems of the iron-group metals with the Group IV and V transition-metal monocarbides. Unlike tungsten monocarbide, which hitherto has been the centre of interest for liquid-phase sintering studies and which has a hexagonal crystal structure, these carbides have a cubic crystal structure.

2. Experimental

2.1. Materials

The compositions of the alloys studied are given in table I. They were prepared by mixing (but not milling) the relevant proportions of the powdered constituents. The powders were of commercial quality with the high purity which is essential for the production of cemented carbides. For example, the cobalt was of 99.9%

TABLE I Composition of investigated alloys.

Alloy	Wt % of stated constituent						
	NbC	Co	TiC	WC	NbB ₂	Nb	Graphite
1	79.00	21.00	—	—	—	—	—
2	77.75	21.00	—	—	1.25	—	—
3	75.25	21.00	—	—	3.75	—	—
4	77.00	21.00	2.00	—	—	—	—
5	74.00	21.00	5.00	—	—	—	—
6	74.00	21.00	—	5.00	—	—	—
7	79.51	19.51	—	—	—	0.98	—
8	78.94	20.98	—	—	—	—	0.08

purity, the main impurity being nickel. The total impurities in the NbC did not exceed 0.5%, excluding up to 2% TaC in solid solution.

The mean particle size of the NbC powder was $\sim 2 \mu\text{m}$ and none of the other powders had particle sizes greater than $5 \mu\text{m}$.

The powders were pressed at 1 metric ton/cm² (1 metric ton = 10^3 kg) into specimens suitable for sintering ($\sim 6 \times 6 \times 6$ mm).

2.2. Sintering

The specimens were sintered in a resistance furnace on substrates formed by small plaques of pressure-sintered NbC. During sintering, a vacuum of 5×10^{-4} to 5×10^{-5} torr was maintained. The sintering temperatures and times of all the specimens are given in table II.

Heating of the specimens was carried out slowly up to 1300° C to allow degassing; the pressure during this stage was not allowed to exceed 6×10^{-4} torr. Heating from 1300° C to the sintering temperature was carried out rapidly (~ 2 min to 1420° C) to avoid excessive grain growth before "zero" time. The furnace was equipped with an optical viewing system and it was possible to determine roughly the temperature at which liquid first appeared in the alloys by observing the shrinkage of the specimens. For the alloys containing NbB₂ this temperature was low ($\sim 1170^\circ$ C), so that there was probably considerable pre-zero grain growth. To observe the state of the microstructure at "zero" time, the alloy with no additions (alloy 1) and the alloy with 3.75% NbB₂ (alloy 3) were heated to the sintering temperature by the normal procedure and then instantly cooled again.

All the specimens were allowed to cool in the furnace, the high vacuum being maintained. To cool from 1420 to 1300° C took 1 min, and from 1420 to 1000° C took 5 min.

Temperature was measured to $\pm 5^\circ\text{C}$ by two thermocouples placed just below the specimen.

At least one specimen of most of the alloys was taken for an oxygen analysis, the results of which are included in table II.

2.3. Metallography

The sintered specimens were sectioned and prepared for metallographic examination. For most purposes a suitable etching reagent was an aqueous solution of 20% potassium hydroxide and 20% potassium ferricyanide.

Quantitative measurements of the microstructure were made on photomicrographs taken from a number of different random areas on each specimen surface, at magnifications of 500, 1000, or 2000, depending on the grain size. Results are based on the measurement of about 1000 grains in each specimen. The binder-phase fraction was determined by a point-grid method recommended by Hilliard and Cahn [5]. The mean intercept length of the carbide grains, the mean free path of the binder phase, and the contiguity of the carbide phase were determined by the random intercept method described by, among others, Exner and Fischmeister [6].

It was found that the greatest source of error in these measurements was due to the finite thickness imparted to the grain boundaries by etching. This led to an error of about $\pm 3\%$ in the measurement of grain size. This was sometimes exceeded by a real deviation caused by the grain-size distribution. The error in the contiguity measurement was at least $\pm 5\%$ because of the uncertainty, in some cases, of whether or not a thin film of cobalt existed between carbide grains.

Grain shape was estimated qualitatively. Myers [7] has shown that certain three-dimensional shapes can be determined, using a statistical approach, from a two-dimensional section through a large number of randomly oriented grains of that shape. In the present study this was not possible because the characteristic grain shape was distorted by impingement of the grains. Nevertheless, the same principle allowed an intuitive, qualitative estimate, sufficient for the classification of shape into: spherical; cubic with rounded edges; angular cubic; polyhedral with rounded edges; angular polyhedral.

The results of all measurements are given in table II*.

*The meaning of the term "contiguity" in the seventh column of table II is defined in section 3.6.

3. Results and Discussions

3.1. General Description of Microstructures

All the alloys, apart from those containing NbB_2 , were two-phase at room temperature. No graphite and no carbides, other than the NbC-based phase, could be detected. Microstructures of two of the alloys are shown in figs. 1 and 2. As seen in table II, the measured binder-phase content was usually below 20 vol % (the approximate nominal value) and

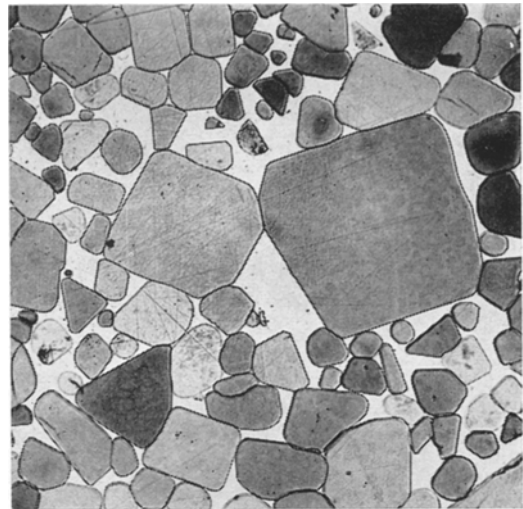


Figure 1 Microstructure of NbC/21 wt % Co alloy (no additions); sintered 120 min at 1420°C ($\times 335$).

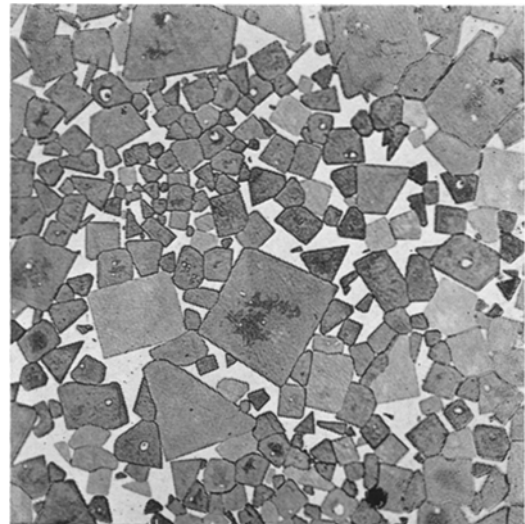


Figure 2 Microstructure of NbC/21 wt % Co alloy with 5 wt % TiC; sintered 120 min at 1420°C ($\times 335$).

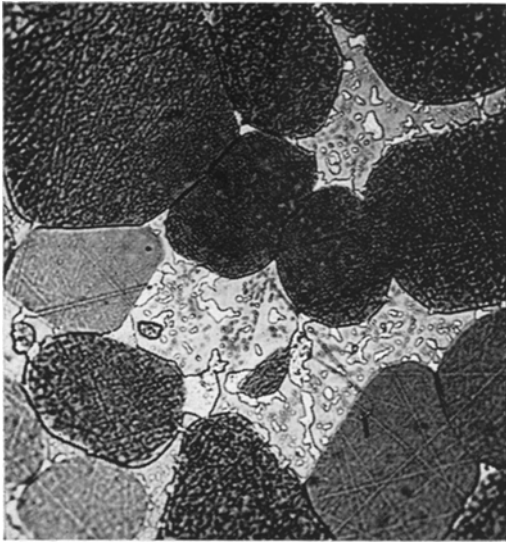


Figure 3 Microstructure of NbC/21 wt % Co alloy with 3.75 wt % NbB₂; sintered 120 min at 1420° C (× 840).

tended to decrease with sintering time, undoubtedly because of evaporation and, to some extent, infiltration into the substrate.

In the alloys which contained NbB₂ the binder phase had a eutectic structure at room temperature (fig. 3). This was probably a pseudo-binary eutectic of cobalt and a boride. Similar eutectics have been reported for the TiB₂/Co system by Samsonov [8], who considered the boride to be TiB₂, and in the TaB₂/Ni system by Lavendel [9], who considered the boride to be Ni₅TaB₂. The formation of such a eutectic explains the low melting point of the binder phase. Because the eutectic constituents are included in the liquid phase at the sintering temperature, the eutectic was considered as part of the binder phase when measurements were made.

TABLE II The conditions of sintering and the microstructural properties of the alloys.

Alloy	Alloying additions (wt %)	Sintering temperature (° C)	Sintering time (min)	Vol % binder phase	Mean grain intercept, \bar{d} (μm)	Contiguity, G	Mfp of binder, L_b (μm)	Oxygen content (ppm)	Grain shape*
1	0	1420	0	17.0	4.8 ± 0.3	0.40	1.65	—	c-r
1	0	1420	15	14.9	9.0 ± 0.3	0.45	2.9	—	c-r & c-a
1	0	1420	29	15.7	11.7 ± 0.3	0.38	3.5	44	c-r
1	0	1420	120	14.2	17.6 ± 0.3	0.43	5.1	—	c-r & c-a
1	0	1420	300	15.8	23.9 ± 0.5	0.36	7.1	57	c-r
1	0	1400	48	17.9	11.8 ± 0.5	0.36	4.4	—	c-r & c-a
1	0	1450	48	17.5	15.5 ± 0.5	0.32	5.0	—	c-r
2	1.25 NbB ₂	1420	50	16.4	15.7 ± 0.5	0.37	4.8	160	p-r
2	"	1420	120	14.3	19.2 ± 0.6	0.40	5.4	—	p-r
3	3.75 NbB ₂	1420	0	21.4	7.2 ± 0.4	0.40	3.2	—	p-r & p-a
3	"	1420	15	18.7	10.0 ± 0.4	0.37	3.7	30	p-a
3	"	1420	48	16.3	13.0 ± 0.5	0.36	4.0	—	p-r
3	"	1420	120	19.3	16.0 ± 0.3	0.33	5.8	86	p-r
3	"	1420	300	13.8	20.2 ± 0.5	0.45	5.9	—	p-r
4	2 TiC	1420	48	15.5	11.2 ± 0.5	0.46	3.9	170	c-a
5	5 TiC	1420	15	18.9	5.0 ± 0.3	0.47	2.25	—	c-a
5	"	1420	48	17.8	7.2 ± 0.3	0.47	2.9	34	c-a
5	"	1420	120	18.0	10.7 ± 0.5	0.42	3.9	87	c-a
5	"	1420	300	11.7	12.0 ± 0.5	0.56	4.0	—	c-a
5	"	1450	48	15.1	9.1 ± 0.5	0.47	3.0	—	c-a
5	"	1480	48	16.1	11.3 ± 0.5	0.43	3.8	—	c-a
6	5 WC	1420	15	17.2	7.4 ± 0.4	0.39	2.5	—	p-r
6	"	1420	50.5	21.1	9.8 ± 0.3	0.33	4.2	96	p-r & p-a
6	"	1420	120	16.3	12.8 ± 0.5	0.39	4.1	—	p-r & p-a
7	0.976 Nb	1420	15	16.8	10.0 ± 0.3	0.40	3.4	63	p-r
7	"	1420	48	16.0	14.0 ± 0.5	0.38	4.4	—	p-r
7	"	1420	120	12.5	17.7 ± 0.3	0.44	5.4	56	p-r
8	0.08 C	1420	51	19.0	12.5 ± 0.5	0.37	4.6	—	c-r & c-a

*c = cubic; p = polyhedral; r = rounded; a = angular.

3.2. Isothermal Grain Growth

The growth of solid particles dispersed in a liquid matrix is considered to occur, in many systems, by a solution/precipitation process (coalescence, another conceivable growth process is discussed later). The driving force for growth is the accompanying reduction in interfacial energy of the system and the process is made possible by the variation in solubility of the particles with the radius of curvature of their interface with the liquid. Growth by the solution/precipitation process can be described theoretically by one of two equations derived by Wagner [4]. These may be written:

$$\bar{r}^3 - \bar{r}_0^3 = \frac{8\gamma_{s1}\Omega^2}{9RT} DC_0t \quad (1)$$

and

$$\bar{r}^2 - \bar{r}_0^2 = \frac{64\gamma_{s1}\Omega^2}{81RT} k_r C_0t \quad (2)$$

where \bar{r} is the mean grain radius after time t , and \bar{r}_0 is the initial mean radius; γ_{s1} is the interfacial energy between solid and liquid per unit area; Ω is the molecular volume of the solid; R is the gas constant and T the absolute temperature; D is the coefficient of diffusion for atoms or molecules of solute in the liquid; C_0 is the solubility of the solid phase in the liquid (adjacent to a plane surface of the solid); and k_r is the rate constant for the reaction involved in the transfer of atoms from solid to liquid.

Equation 1 applies when the process is controlled by the diffusion of atoms or molecules of the solid phase in the liquid and equation 2 when the process is controlled by the rate at which the atoms or molecules of the solid leave the solid/liquid interface. Both equations imply a number of conditions which are not fulfilled for liquid-phase-sintering systems; for example, sphericity of the particles, non-contiguity of the solid phase and stoichiometry of the solid, if it is a compound. Furthermore, equation 1 is based on the assumption that the diffusion zone of any particle does not overlap those of neighbouring particles and thereby affect their normal dissolution or growth rate [10].

Equations 1 and 2 may be written in a more general form:

$$\bar{r}^n - \bar{r}_0^n = K_a t \quad (3)$$

*In equation 5, \bar{r}_0 cannot be neglected. Differentiation shows that equation 5 implies that the rate of grain growth is dependent on the amount of growth that has occurred rather than the actual grain size. This in turn implies that during sintering the alloy must "remember" its original grain size. It is also implied that when $t = 0$ the rate of growth is infinite.

where $n = 2$ or 3 and K_a is a temperature-dependent constant for a given system. In many cases, the above-mentioned departures from the Wagner model will only affect the value of K_a and if they remain constant during sintering, the grain growth should still be described by equation 3 but with K_a a semi-empirical constant.

When \bar{r}_0 is small compared to \bar{r} the grain growth may be described by the equation:

$$\bar{r}^n = K_a t \quad (4)$$

Experimental results on a number of different systems have confirmed the applicability of equations 3 or 4. For example Sarian and Weart [10] showed that equation 4, with $n = 3$, is valid for the grain growth in the NbC/Fe system. When boron is present as an impurity in the system n becomes 2. They derived a factor to allow for the overlapping of particle diffusion zones at low liquid fractions but found experimentally that this was unnecessary - i.e. K_a was independent of liquid fraction - between 10 and 40 vol % iron. Because of lack of knowledge of interfacial energies, diffusion coefficients or interface reactions, it is not possible to confirm the Wagner equations precisely. Nevertheless the results of Lenel [11] for the Fe/Cu system agree well with equation 1 if known values of γ_{s1} and D for that system are applied [10].

Another theoretical equation describing grain growth has been derived by Exner and Fischmeister [12], assuming a solution/precipitation process controlled by an interface reaction. This is

$$(\bar{r} - \bar{r}_0)^2 = K_b t \quad (5)$$

where K_b is a temperature-dependent constant. This equation implies an entirely different time-dependence of grain growth than do equations 3 or 4*. Results for the WC/Co system are in good agreement with equation 5 rather than equation 3 [13]. It is an unfortunate fact, however, that a set of results which agree with an equation with the form of equation 3 having $n \geq 3$, will sometimes simultaneously agree with equation 5. Some examples of this are pointed out by Exner and Fischmeister [12]. An unambiguous interpretation of such results is at present not possible.

The grain growth of NbC in cobalt, observed in this investigation, is in very close agreement with equation 3 with $n = 3$. This is shown in

fig. 4 by plotting the grain size, \bar{d} (\bar{d} is the mean intercept length of the carbide grains and is a constant function of \bar{r} for a fixed grain shape) on a \bar{d}^3 scale, against sintering time. The results give a linear plot which intersects the \bar{d} -axis at \bar{d}_0 . The results indicate that \bar{d}_0 is negligible so that equation 4 is also valid and a plot of $\ln \bar{d}$ versus $\ln t$ should be linear with a slope of $1/n$. This is confirmed in fig. 5, the slope of the plot being $1/3$.

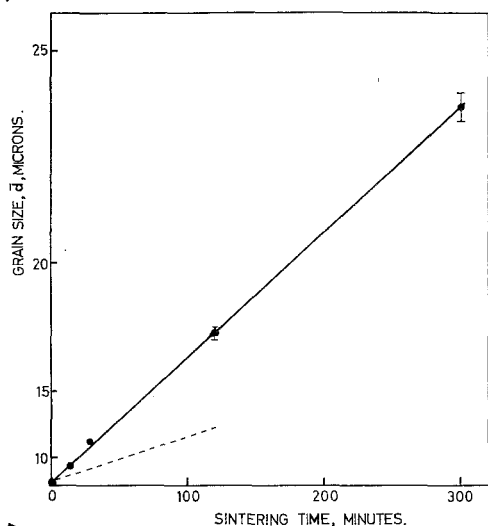


Figure 4 Grain growth of carbide phase in NbC/21 wt % Co alloy (no additions) at 1420° C – plotted as \bar{d}^3 versus t , showing that $\bar{d}^3 - \bar{d}_0^3 = Kt$. The dotted line is for the alloy with 5 wt % WC added (see also fig. 7).

It follows from the above discussion that these results suggest that the grain growth of NbC in liquid cobalt occurs by a diffusion-controlled solution/precipitation process, as is the case in the NbC/Fe system [10]. The values of D , C_0 , and γ_{s1} for the NbC/Co system are not known but the observed growth rate is in approximate agreement with the Wagner model if probable values (to within an order of magnitude) of these parameters are assumed.

The coarsening of \bar{L}_b , the mean free path in the binder phase, is also represented in fig. 5. and is seen to have a similar time-dependence to the grain size. This is to be expected for, as can be shown theoretically, \bar{L}_b is directly proportional to the grain size of the dispersed phase for a given binder fraction and contiguity (see section 3.6).

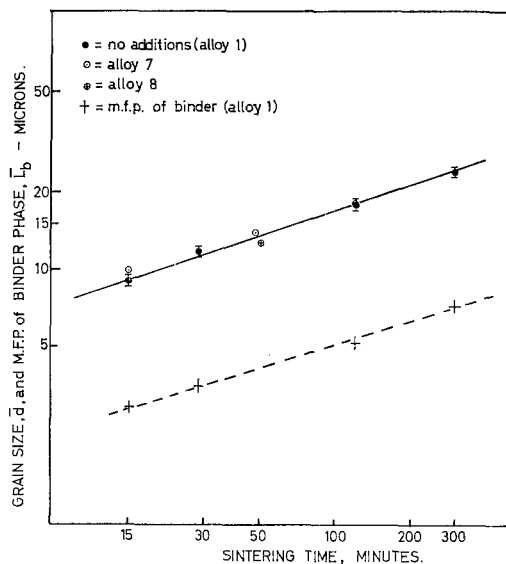


Figure 5 Grain growth of carbide phase and growth of mean free path of binder phase in NbC/21 wt % Co alloys with different niobium : carbon ratios, at 1420° C – plotted as $\ln \bar{d}$ versus $\ln t$, showing that $\bar{d} \sim Kt^{1/3}$.

3.3. The Effect of Temperature on Grain Growth

The rate of grain growth is often considered to increase exponentially with temperature and is described by the Arrhenius equation, thus

$$K_a = K_0 \exp(-Q/RT) \quad (6)$$

where Q is the “activation energy” of grain growth and K_0 is a constant. The rate constant K_a , however, contains a number of temperature-dependent terms which are not kinetic in nature and/or are not exponentially dependent on temperature. Therefore, interpretation of the “activation energy” value must be made with caution. This parameter can, nevertheless, sometimes indicate the mechanism of grain growth. Thus Exner and Fischmeister [13] found a value for Q of 142 kcal/mole for the WC/Co system. This is in good agreement with Skolnick’s [14] value for the activation energy of solution of WC in cobalt and so supports the suggestion that the growth in this system is interface-reaction controlled.

The effect of temperature on the grain growth of NbC in cobalt is shown as an Arrhenius diagram in fig. 6. The rate constant is here represented by t_c , the time required to reach a fixed grain size. If it is assumed that the mechan-

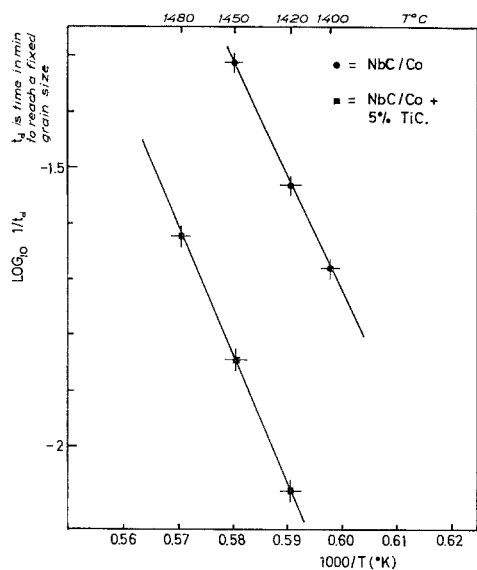


Figure 6 Effect of temperature on the grain growth of NbC/21 wt % Co alloys; (i) no additions, (ii) 5 wt % TiC added - plotted as an Arrhenius diagram. Growth rate is represented by the time to reach a fixed grain size; $\bar{d} = 11.8 \mu\text{m}$ for (i) and $10.7 \mu\text{m}$ for (ii).

ism of growth does not change with temperature, then the activation energy for growth is 95 ± 15 kcal/mole. This value is surprisingly high for a mechanism controlled by diffusion in a liquid phase, since the activation energy for diffusion in liquids rarely exceeds 20 kcal/mole.

3.4. The Effect of Alloying on Grain Growth

Barely any quantitative information exists on the effect of small alloying additions on grain growth during liquid-phase sintering. It can be supposed, however, that alloying can affect growth both by changing the growth mechanism (i.e. by changing n) and by changing the rate constant, K_a . An example of the first effect is the change of growth in the NbC/Fe system, from a diffusion-controlled mechanism to one controlled by an interface reaction, caused by a trace of boron [10]. By changing one or more of the terms included in K_a (e.g. grain shape, γ_{sl} , C_0 and D or k_r), almost any addition might alter the grain growth. The extent to which this occurs is still a matter of speculation.

The present investigation has shown that additions of WC and TiC inhibit the grain growth of NbC in cobalt. The growth for the WC-containing alloy agrees most closely with

equation 3 with a value of $n = 3$ (fig. 7). Thus, the addition of 5 wt % WC to the NbC/Co alloy does not affect the mechanism of grain growth but reduces the growth rate by a factor of about 2. This could conceivably be because the high solubility of WC in cobalt suppresses the solubility of NbC. Similarly the presence of WC may reduce the diffusion of NbC.

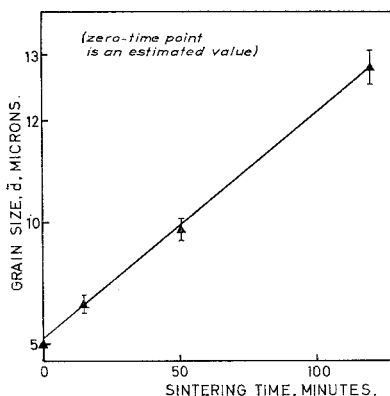


Figure 7 Grain growth of carbide phase in NbC/21 wt % Co alloy with 5 wt % WC, at 1420°C - plotted as \bar{d}^3 versus t , showing that $\bar{d}^3 - \bar{d}_0^3 = Kt$.

The effect of TiC on the grain growth is not quite as clear because the results do not agree with any of the above equations. For sintering times up to 120 min however, the growth agrees closely with equation 3 with $n = 2$, particularly if \bar{d}_0 is assumed to be little greater than the particle size of the original powder (fig. 8). This result implies that the TiC inhibits the rate at which NbC enters the liquid and so the grain growth becomes controlled by the interface "reaction". The effect of temperature on the growth rate of the alloy with 5 wt % TiC is shown in fig. 6. The activation energy for grain growth is 107 ± 15 kcal/mole (assuming $n = 2$ for the whole temperature range). This high value is consistent with an interface-reaction controlled mechanism. The retardation of growth in this alloy at longer sintering times may be caused by a change to the diffusion-controlled process or may be associated with the sudden decrease in binder fraction and consequent increase in contiguity which was observed (table II). The latter possibility is considered below with regard to coalescence.

The additions of NbB_2 do not greatly affect the isochronal grain size of NbC in cobalt but

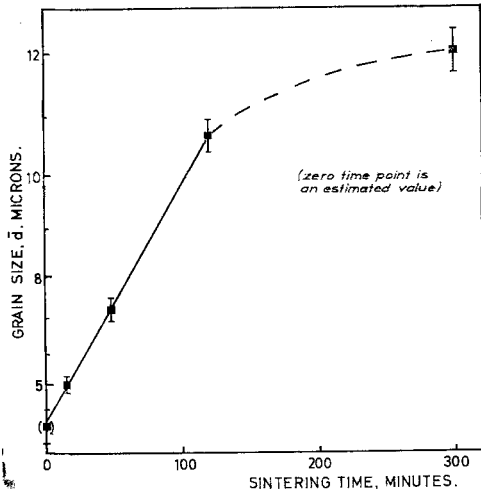


Figure 8 Grain growth of carbide phase in NbC/21 wt% Co alloy with 5 wt% TiC, at 1420° C - plotted as \bar{d}^2 versus t , showing that $\bar{d}^2 - \bar{d}_0^2 = Kt$ for the first two hours.

have a surprising effect on the growth mechanism. The grain growth agrees with equation 3 for a value of $n = 4$ (fig. 9), suggesting that the

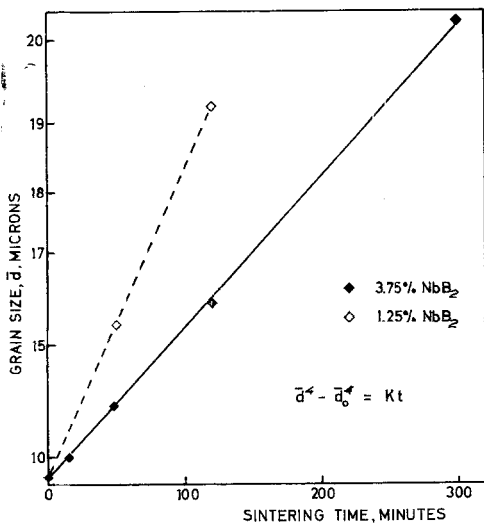


Figure 9 Grain growth of carbide phase in NbC/21 wt% Co alloy with NbB₂ additions, at 1420° C - plotted as \bar{d}^4 versus t showing that $\bar{d}^4 - \bar{d}_0^4 = Kt$ (compare with fig. 10).

solution/precipitation processes described by equations 1 and 2 do not occur in this case. It is of interest that the same growth law has been observed, for the growth of nickel grains in the

*It is often observed during cemented carbide production, that there is a connexion - either direct or incidental - between structure coarseness and the carbon content of the alloy.

presence of an intergranular liquid Ni/S eutectic, by Smith and Spencer [15]. They attributed the time exponent of 1/4 to a process involving interfacial diffusion. It is conceivable, in the present case, that NbB₂ inhibits the solution of NbC, at the same time enhancing its interfacial diffusion. The results for the NbB₂ alloys, however, cannot be interpreted unambiguously, for they also agree fairly well with equation 5 as seen in fig. 10. The theory of Exner and Fischmeister suggests that this equation describes the solution/precipitation process controlled by an interfacial reaction.

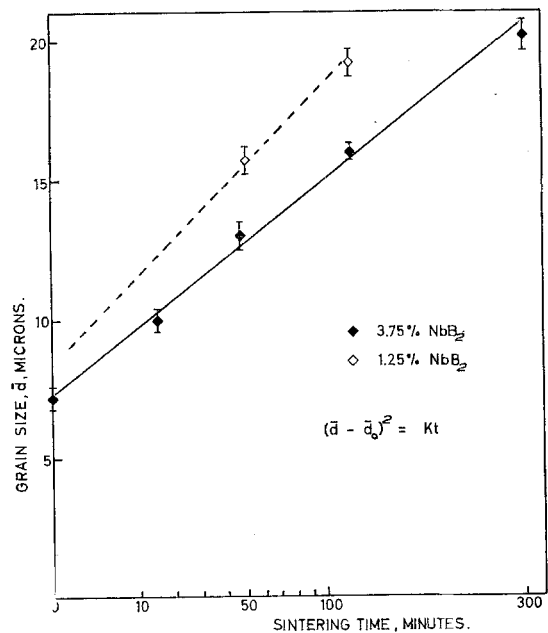


Figure 10 Grain growth of carbide phase in NbC/21 wt% Co alloy with NbB₂ additions, at 1420° C - plotted as \bar{d} versus $t^{\frac{1}{2}}$, showing that $(\bar{d} - \bar{d}_0)^2 = Kt$.

Another composition variable, which was studied in the present investigation, is the niobium/carbon ratio in the alloy. This ratio might be expected to affect the grain growth if one of the constituent elements controls the transport of NbC "molecules"*. As seen in fig. 5, the change in grain size produced by the addition of niobium metal or graphite was barely significant. Larger alterations in the ratio, however, might have had a greater influence.

3.5. The Coalescence Process

The process of coalescence is considered by many authors to play an important part in grain growth during liquid-phase sintering [13, 16] but, because of lack of definition, the term *coalescence* has occasioned some confusion. The concept of coalescence probably first took firm root after the presentation of the "coalescence hypothesis" by Humenik and Parikh [17]. They considered that the extreme grain growth in such systems as TiC/Ni and WC/Cu could not be satisfactorily explained by a solution/precipitation process because the solubility in these systems was so much lower than in such systems as WC/Co which exhibited much finer structures. They suggested rather that, because of poor wetting of the solid by the liquid in these systems, groups of grains "coalesced" to form larger "grains". They then qualified this by pointing out that these large "grains" were, in fact, frequently clusters of smaller grains. Thus their judgement of coarseness was based on *agglomerate* size rather than on real grain size, and so the coalescence process as defined by them cannot be directly applied to grain growth as measured quantitatively. It follows that a distinction must be made between: (i) coalescence meaning the combination of two or more grains to form an agglomerate in which the grains retain their separate identity (i.e. are separated by contiguous boundaries), and (ii) coalescence meaning the combination of two or more grains to form a single grain (i.e. with a single lattice orientation). It is the latter process which would contribute to grain growth and is, in this study, referred to as "coalescence". The first process being termed "agglomeration".

If coalescence does occur, it is clear that equations 1 and 2 will not describe overall grain growth, and the deviation from the growth laws expressed by equations 3 or 5 will depend on the relative contribution and the time-dependence of coalescence. Unfortunately, it is rather difficult to determine experimentally the part played by coalescence, because grains rarely show evidence of their growth history. One sign of coalescence, however, is considered to be the presence of spheres of binder phase, trapped within solid-phase grains [13, 18]. Exner and Fischmeister [13] observed such spheres in WC/Co alloys and assumed that coalescence contributed significantly to the grain growth, but they did not treat the subject quantitatively.

In the present investigation the alloys were

studied with the object of determining the extent and mechanisms of coalescence. The presence of entrapped spheres of cobalt, especially in the TiC-containing alloys (fig. 2), suggested that coalescence did occur. Observations in the present study and results for other systems provide a basis for the following suggested model for coalescence:

It is first helpful to divide systems into those which exhibit poor wetting, such as WC/Cu, and those which exhibit fairly good wetting such as Nb/Co and WC/Co (the significance of wetting is discussed in the next section, 3.6). In the first type of system, comparatively large agglomerates of grains form. The liquid phase is almost completely excluded from these agglomerates and many of the grains are almost entirely surrounded by other grains. If such grains are to grow, they must do so by coalescence, which in this case will be the same as solid-state grain growth (fig. 11a).

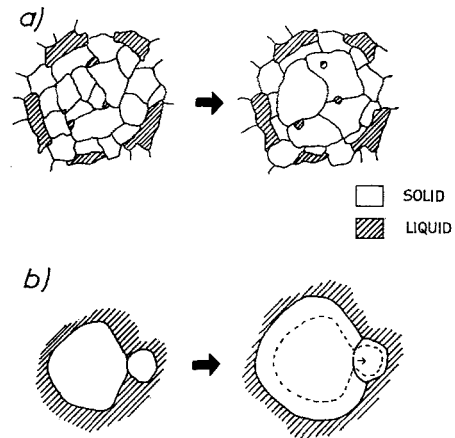


Figure 11 Illustrating possible grain-coalescence processes (a) in a system of poor wetting, (b) in a system of good wetting.

In a system which exhibits good wetting, agglomerates of more than a few grains, and which exclude liquid phase, are probably rare. Consequently, a large proportion of the surface of almost every grain is free to grow by a solution/precipitation process. Even at room temperature, when the contiguity is expected to be higher, this is seen to be the case (figs. 1 and 2). Coalescence could occur, however, as follows. A pair of grains of different radius will normally grow at a different rate and so, if they have a mutual, contiguous boundary, it becomes

curved. That this actually occurs is clearly seen in fig. 12. According to a law of solid-state grain growth, such a boundary will move

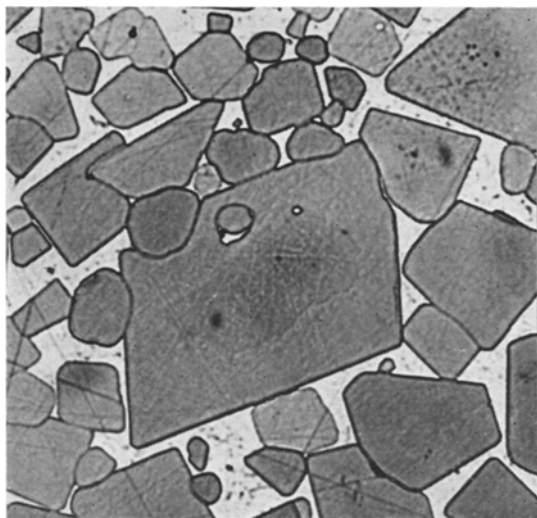


Figure 12 Showing the presence of curved, carbide grain-boundaries and the formation of trapped cobalt spheres. (Alloy 4, sintered 48 min. at 1420° C, × 840.)

towards its centre of curvature; thus coalescence will occur by the "digestion" of the smaller grain by the larger (fig. 11b). Unlike the case for the poor-wetting system, the movement of the solid-solid boundary depends on the movement of the adjacent solid/liquid interfaces. Therefore, even if atom transport in the solid phase were faster than that through the liquid, coalescence could not *increase* the overall grain growth rate.

Since, in both systems, the coalescence occurs by a solid-state grain-growth mechanism, it is possible to describe the overall grain growth, in both cases, by the following, single equation:

$$\bar{r} = \mu K_1 t^{1/n_1} + (1 - \mu) K_2 t^{1/n_2} \quad (7)$$

where μ is the effective fraction of the grains which is growing by solid/liquid interface movement, with a rate constant of K_1 and a time exponent of $1/n_1$; and the remaining grain-

fraction is growing by a solid-state growth mechanism, with rate constant K_2 and time exponent $1/n_2$. It is here assumed that the initial grain size is negligible and that equations of type 4 are valid for both growth processes*.

The value of the fraction, $1 - \mu$, will depend to a large extent on the contiguity of the solid phase at the sintering temperature.

If equation 7 is valid, it follows that the observed grain growth of a system will depend on the value of μ and the relative magnitudes of K_1 , K_2 , n_1 , and n_2 . For example, in systems for which μK_1 and $(1 - \mu) K_2$ are similar in magnitude and n_1 and n_2 are different, grain growth represented by equation 4 will not be observed and the plot of $\ln \bar{r}$ versus $\ln t$ will not be linear. If, however, $n_1 = n_2$ (n for solid-state grain growth is often found to be 2 or 3), an equation of type 4 will apply, if the initial grain size is negligible, but the rate constant, K_a will, represent more than one mechanism.

In systems of good wetting, if $(1 - \mu) K_2 > \mu K_1$, equation 7 will not apply, for, as discussed above, coalescence cannot increase the overall grain growth of such systems. For poor-wetting systems, however, this is not so and in a system like WC/Cu, in which K_1 and μ are relatively low, the solid-state growth (i.e. coalescence) might be the dominant growth process.

If the above model is applicable, the precise interpretation of grain-growth measurements of many systems will be difficult, because variables in equation 7 cannot be determined. It is felt, however, that coalescence contributes little to the growth in the alloys of this investigation, with the exception of those containing TiC, and therefore that the measurements made represent solution/precipitation processes to a good approximation. This is considered to be so because the good wetting of the carbide by the cobalt gives a low value of $(1 - \mu)$ and also because the mobility of the solid/solid boundaries is considerably lower than that of the solid/liquid boundaries (i.e. K_2 is small compared with K_1). This latter fact is suggested by observation of the microstructure of the alloys. For

*If the effective number of grains growing by the first process is N_1 and by the second process N_2 , then N_1 grains have the mean size:

$$\bar{r}_1 = K_1 t^{1/n_1}$$

and N_2 have the mean size:

$$\bar{r}_2 = K_2 t^{1/n_2}$$

Therefore the overall mean size is:

$$\begin{aligned} &= \frac{N_1 K_1 t^{1/n_1} + N_2 K_2 t^{1/n_2}}{N_1 + N_2} \\ &= \mu K_1 t^{1/n_1} + (1 - \mu) K_2 t^{1/n_2} \end{aligned}$$

example fig. 12 shows solid/solid boundaries of high curvature. A low rate of solid-state grain growth for NbC is also indicated by the results of Ordan'yan and Avgustinik [19].

The failure of the alloy containing 5% TiC to conform to any of the theoretical rate laws may be attributed to the sharp fall in liquid-phase fraction, at longer sintering times, which caused a corresponding increase in contiguity (table II) and consequently, an increase in $(1 - \mu)$.

That coalescence is encouraged by high contiguity is also suggested by the fact that the TiC-containing alloys, which had higher contiguities than the other alloys (see next section), also exhibited the most spheres of entrapped cobalt. The formation of these spheres can be understood with the aid of fig. 12. A small volume of cobalt is trapped between two or more contiguous grains; the grains coalesce by movement of the contiguous boundary but the cobalt remains, becoming spherical to reduce interfacial energy.

In the above discussion of the coalescence process, it has been assumed that it occurs by atom transport. It should be mentioned, however, that it is also conceivable that the lattices of grains could align by the relative movement of complete grains [20]. Such a process might be possible during the first few minutes of sintering, for, as shown by Kingery [21], there is strong evidence to suggest that a "rearrangement" of the solid particles occurs at this stage. To observe such a process and describe quantitatively its effect on grain growth would be difficult.

3.6. Contiguity

The *contiguity* of a phase is defined as the average fraction of the surface area shared by one grain of the phase with all neighbouring grains of the same phase [16]. It is a parameter which helps to describe quantitatively the distribution of phases in an alloy and is a property which normally influences the mechanical properties of the alloy. It is usually measured at room temperature but this value may be taken as an indirect indication of the sintering-temperature contiguity which, as discussed in the previous section, is a parameter possibly significant in grain growth.

Before discussing the results of this investigation, it is helpful to note two factors which are known to affect the contiguity of this type of alloy.

(i) *Wetting*. The contiguity of the solid phase *during sintering* is affected by the relative values of the solid/solid and solid/liquid interface energies. Thus, two adjacent grains will become contiguous on those areas of contact for which the condition is fulfilled:

$$\gamma_{ss} < 2\gamma_{sl}$$

where γ_{ss} is the energy of the contiguous boundary (its value will depend on the relative lattice orientation of the two grains). The lower the value of γ_{sl} relative to the γ_{ss} values of a system, the greater the penetration is of the liquid between the grains and therefore the lower is the contiguity. This contiguity at the sintering temperature will be modified (probably increased), by precipitation of solid phase from the liquid, when the alloy cools.

(ii) *Binder-phase content*. For a given system, contiguity decreases with increasing binder-phase fraction. This effect has been studied in the TiC/Co system [16], the WC/Co system [13] and also for a system of silver spheres in a plastic matrix [22]. The contiguity when no binder phase is present is unity. The fall in contiguity, produced by a given change in binder fraction, is greatest at low fractions and decreases as the binder fraction increases. It is to be expected that the sensitivity of contiguity to binder fraction at low fractions (i.e. fractions commonly used in liquid-phase sintering), increases with the wettability of the solid.

The results of contiguity measurements on the alloys of this investigation are given in table II. No clear relationship between the contiguity and sintering conditions is apparent, mainly because of the variations in the binder fraction, α between specimens. To reveal the possible effects of sintering conditions, it is necessary to separate the effect of binder fraction. The contiguity values can be "normalised" with respect to α , if a simplifying assumption is made; namely, that the contiguity, G , for a given system, is proportional to $(1 - k\alpha)$, where k is a constant for the system. This is approximately true for narrow intervals and low values of α . Remembering that $G = 1$ when $\alpha = 0$, it follows from this assumption that:

$$G_2 = 1 - \alpha_2(1 - G_1)/\alpha_1 \quad (9)$$

where G_1 and G_2 are the contiguities for the binder fractions α_1 and α_2 respectively.

The contiguity for a binder fraction of 0.2, calculated with equation 9, is shown for the

different alloys as a function of sintering time and sintering temperature in figs. 13a and b.

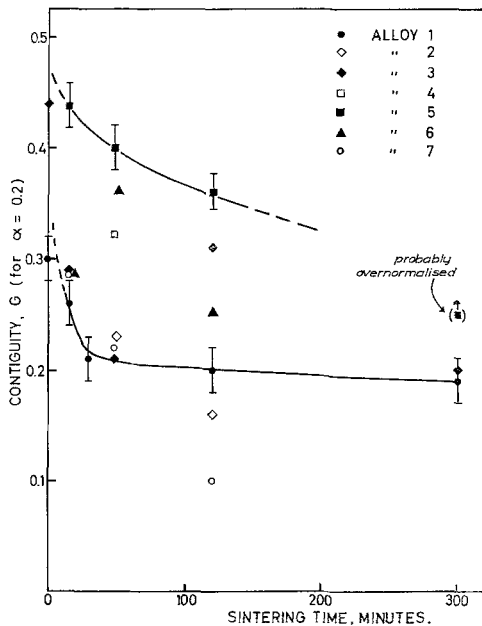


Figure 13a Effect of sintering time at 1420°C on the carbide contiguity of NbC/Co alloys with 20 vol% binder phase. (The measured contiguity was corrected to $\alpha = 0.2$ using equation 9.)

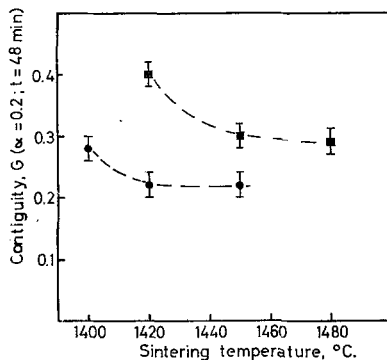


Figure 13b Effect of sintering temperature on the carbide contiguity, at 48 min sintering time and 20 vol% binder phase of two NbC/Co alloys; (i) without additions, (ii) with 5 wt% TiC added.

Despite the scatter of results, which is partly due to the measurement difficulty discussed in section 2.3, it is clear that contiguity – at a constant binder content – tends to decrease with increasing sintering time and temperature. The decrease is most marked during the first

minutes of sintering, and at longer sintering times there is a tendency towards a constant contiguity. This suggests that, during the early stages of sintering, a process of carbide deagglomeration occurs. The observed effect of temperature may only reflect the increased rate of this process at higher temperatures. Exner and Fischmeister found the same effects with a WC/10% Co alloy [13]. Gurland, on the other hand, also investigating WC/Co alloys, observed an increase in contiguity during sintering [16]. He concluded that this was evidence that there is an increased tendency for grains to coalesce as sintering proceeds. The results of the present investigation, supported by those of Exner and Fischmeister, suggest that this is not so, unless a third factor such as evaporation of the binder phase is involved. The results of Exner and Fischmeister are possibly more reliable because they were obtained using electron microscopy with a consequently better resolution [6]. For the NbC/Co alloys the problem of optical resolution was not so acute because the microstructures were so much coarser.

A further observation in the present study is that the contiguity of the alloy containing 5% TiC is significantly higher than that of the other alloys. This can be explained, at least partly, by differences in grain shape. It can be shown that grains of a given volume, enclosed in a given volume, will “overlap” each other to an extent dependent on their shape. For example, grains of cubic equilibrium shape will overlap more than spherical grains. The grains in the TiC-containing alloys are cubic and more angular than in the other alloys; therefore, if other factors such as wettability and binder fraction are the same, the contiguity of the TiC-containing alloys is expected to be higher. It is, nevertheless, also possible that the TiC addition reduces the wetting in the system by reducing the value of γ_{ss} relative to that of γ_{sl} .

3.7. Grain Shape

The effect of grain shape on the properties of liquid-phase sintered alloys has been discussed briefly by Humenik and Whalen [23], but little research has been carried out on this subject. It was shown in previous sections, however, how grain shape might affect contiguity and grain growth, and it may thereby indirectly influence properties. Even if grain shape is not of practical interest, it is of some theoretical interest.

The results of the study of grain shape of the NbC/Co alloys are summarised in table II. The basic grain shape of the system is cubic modified by rounding of the cube edges (fig. 1). This shape, however, is very sensitive towards minor alloy additions. The addition of TiC causes a marked development of the {100} faces of the grains, which thereby become sharp-edged (fig. 2). Additions of WC or NbB₂ alter the cubic form of the grains by causing the development of other faces; it was not possible to determine which. The different alloys maintained their characteristic grain shape throughout sintering. Although the alloys have a characteristic, non-spherical grain shape, there is, in their microstructure, always a small proportion of near-spherical grains of less than the average grain size. These could result from the plane of cross-section passing through grain corners, but it is felt that many of them are true spheres.

These observations are in good agreement with observations on similar systems. Whalen and Humenik [24] have reported that TiC – a cubic carbide like NbC – when sintered with cobalt or nickel, exhibited angular or rounded, cubic or polyhedral grain shapes depending on sintering conditions. They concluded that the presence of oxygen caused rounding of the grains. Sarian and Weart [25] showed that, for NbC in liquid iron, there exists a very narrow temperature range (about 1725° C) above which the NbC grains are nearly spherical and below which they are relatively sharp-edged cubes. They found that impurities of boron, oxygen and nitrogen lowered the transition “temperature”. They also observed the presence of a proportion of spherical grains although the majority shape was cubic.

That grains take up characteristic, non-spherical shapes is due to the anisotropy of the interfacial energy of the crystal. For example, the interfacial energy of the {100} planes of the NbC crystal in liquid cobalt or iron is much lower than that of the other planes. The precise way in which the anisotropy determines shape is predicted by the theorem of Wulff, as has been discussed by Herring [26]. The extreme sensitivity of the shape towards sintering conditions – e.g. temperature and impurities – can also be explained in terms of the Wulff model.

By making a simplifying assumption, a more direct though less general approach than that of Wulff can be used to describe quantitatively the sensitivity of shape, for the specific case of the

cube \rightleftharpoons sphere change. This is as follows:

The volume of a cubic grain of side a and corner radius r (fig. 14) can be shown to have, to a good approximation, a volume:

$$V = a^3 - 2.5752ar^2 + 1.3392r^3 \quad (10)$$

When $r = a/2$ the grain is a sphere, and when $r = 0$ it is a pure cube.

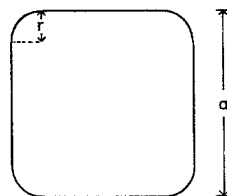


Figure 14 Section of cubic grain with rounded edges.

It is now assumed that the interfacial energy per unit area of the curved surfaces of the grain can be represented by a mean energy, γ_{s1} . If the ratio of the interfacial energy per unit area of the {100} planes to γ_{s1} is β , then the {100} energy is $\beta\gamma_{s1}$. It can be shown that, with these values, the interface energy of the rounded grain is given by:

$$E = 6a^2\beta + r^2(24\beta - 8\pi) + ra(6\pi - 24\beta) \quad (11)$$

The equilibrium grain shape for a given β is given by those r and a values which give a minimum value to E/V (i.e. the interface energy per unit volume) and simultaneously satisfy equation 10, the grain volume, V , being a constant. To solve precisely these simultaneous conditions for a and r at various β values is somewhat tedious. Solving to a fair approximation, however, yields the result illustrated in fig. 15, which shows how grain shape, measured in terms of r and r/a , varies with β . The result is valid for any grain volume but r in fig. 15 is that for unit volume.

The result indicates that, for a ratio of β above 0.85, the grain shape is very close to spherical. In the narrow range of β from 0.85 to 0.80, the shape changes from near-spherical to almost perfectly cubic. For values of β less than 0.79, the grain shape is theoretically a perfect cube. The theory implies, however, that the surface energy is independent of the surface curvature. This is not true for very low values of radius of curvature, for then γ_{s1} increases with decreasing r . Thus r never reaches zero and the curve of r versus β becomes asymptotic towards

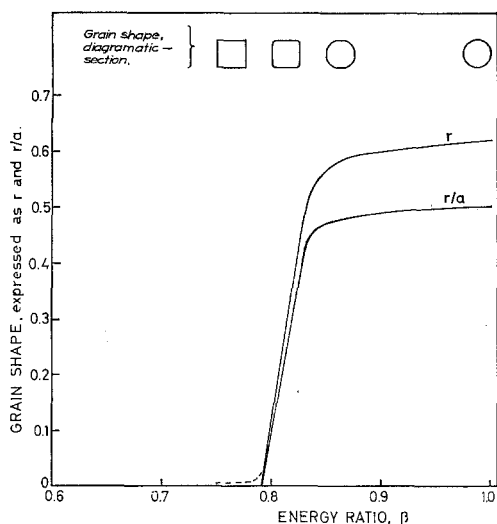


Figure 15 The effect, on the equilibrium shape of a grain, of β , the ratio of the interfacial energy per unit area on the $\{100\}$ planes, to the mean interfacial energy per unit area (assuming no planes besides $\{100\}$ have energies significantly lower than the mean). The shape is expressed as r and r/a (see fig. 14) for a grain of unit volume.

the β -axis as indicated by the dotted line. For the grain sizes of interest here, this effect is probably negligible and it follows from the results illustrated by fig. 15 that the grain shape is extremely sensitive to the relative values of the interfacial energies, within a certain range. The small relative changes in the interfacial energies necessary to cause the sharp shape-change could easily be brought about by small impurity additions or small temperature changes.

The presence of spherical grains in a microstructure in which the majority shape is cubic has been explained qualitatively by Sarian and Weart [25]. The explanation is based on the theory of Wagner which suggests that grains larger than the critical size (that size for which the grain neither grows nor dissolves) grow relatively slowly, whereas those smaller than the critical size dissolve relatively rapidly. Sarian and Weart suggest that the shape of the small grains is governed by kinetic factors rather than surface energy equilibrium and therefore they assume a spherical shape.

4. Conclusions

The following conclusions may be drawn from the results of the present investigation.

The grain growth of the NbC phase during the liquid-phase sintering of the alloy NbC/21 wt % Co at 1420° C is in good agreement with the theory of Wagner [4] for the case of growth by a solution/precipitation process, controlled by volume-diffusion in the liquid phase. The growth can be expressed by the equation:

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

where K is a temperature-dependent constant for which the empirical "activation energy", between 1400 and 1450° C, is 95 ± 15 kcal/mole. Observation of the alloy suggested that grain coalescence contributes little to the overall grain growth. The contiguity of the carbide phase falls sharply during the first minutes of sintering and tends towards a constant value at longer sintering times, if the binder-phase fraction remains constant. The equilibrium grain shape of non-contiguous grains is cubic, modified by rounding of the cube edges.

The addition of 5 wt % WC to the alloy does not affect the growth mechanism but inhibits grain growth by reducing the rate constant, K , by a factor of about two. The addition does not significantly affect the carbide contiguity but does alter the equilibrium grain shape.

The addition of 5 wt % TiC to the alloy sharpens the cubic shape of the grains, increases the room-temperature contiguity, and inhibits the grain growth. The grain growth of the alloy, for long sintering times, did not agree with any single theoretical growth law. This is thought to be because more than one growth mechanism was involved. The growth during the first two hours of sintering could be described by the equation

$$\bar{r}^2 - \bar{r}_0^2 = Kt$$

where K has an "activation energy" of 107 ± 15 kcal/mole in the range 1420 to 1480° C. This suggests a solution/precipitation growth process controlled by an interface-reaction. For longer sintering times, it is thought that, because of increased contiguity brought about by cobalt evaporation, the coalescence process played an increasing part in the growth. Assuming that growth by coalescence was much slower than that by the solution/precipitation process, this would explain the observed reduction in growth rate at longer sintering times.

The addition of up to 3.75 wt % NbB₂ to the alloy changes the grain growth mechanism

in such a way that the growth can be described by the equation

$$\bar{r}^4 - \bar{r}_0^4 = Kt$$

The results are ambiguous, however, and can also be described by the equation

$$(\bar{r} - \bar{r}_0)^2 = Kt$$

which, according to the theory of Exner and Fischmeister [12], represents a solution/precipitation process controlled by an interface reaction. Further study would be necessary to resolve the true mechanism. The addition of NbB₂ also changes the carbide grain shape but does not significantly affect the contiguity.

The extreme sensitivity of grain shape towards sintering conditions and impurities which is observed generally, in liquid-phase sintered alloys, can be explained in terms of the degree of anisotropy of the interfacial energy of the grain.

Acknowledgements

The author would like to thank the company of Stora Kopparbergs Bergslags AB (Sweden) for permission to publish the results of this investigation. Thanks are also extended to Övering B. O. Waller and Dipl Ing P. B. Anderson for the interest they took in the work.

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