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ANOMALOUS SINTERING BEHAVIOR IN THE 95% W-3.5% NI-1.5% Fe COMPOSITE

by

Eugene G. Zukas and Haskell Sheinberg

ABSTRACT

During liquid-phase sintering of W-Ni-Fe composites, single crystal spheroids of essentially pure tungsten form in a W-Ni-Fe matrix. These spheroids grow in a systematic way if either the sintering time is increased, or if the sintering temperature is raised. The generally accepted mechanism of spheroid growth is the dissolution of the small spheroids with simultaneous reprecipitation of tungsten from the molten matrix onto the larger ones, the reaction being driven by surface energy differences between the small and large spheroids. It has been shown theoretically that for such reactions, the plot of log diameter-log time will give a straight line of slope 1/3. This theory has been modified to include a rearrangement process for achieving densification during the early stages of sintering and a coalescence process for combining solid spheroids during the latter stages of sintering. Furthermore, sintering at different temperatures should proceed with a single-valued activation energy since a single growth mechanism is rate controlling.

We studied the sintering behavior of a low volume matrix alloy (95% W-3.5% Ni-1.5% Fe) and found that the slope of the log diameter-log time plot was less than 1/4, and that the growth process could not be represented by a single-valued activation energy. These experiments as well as those generally published in the literature have several shortcomings in that they do not consider the effect of solid state reactions during presintering, nor the effect of sintering temperature on the spheroid nucleation size. Furthermore, determining activation energies after a constant sintering time does not evaluate structural differences. To overcome these objections, we ran a second series of experiments where the baseline material had already been liquid-phase sintered, and the growth rates determined after additional sintering. Activation energies were determined from the times required at the different sintering temperatures to achieve equivalent structures. In these tests, the log diameter-log time plots had slopes less than 1/4 and the activation energies were different for different sintering conditions. These results indicate that the dissolution-reprecipitation process is not rate controlling in the 95% W-3.5% Ni-1.5% Fe composite. We feel that the growth rates are too fast for such a process to be rate controlling, and that "coalescence", i.e., the joining of two or more spheroids that come into contact at the proper crystallographic orientation and form a single spheroid, is much more important even during the initial stages of sintering. The rate for such a growth mechanism would depend on some degree of matrix circulation, and the probability for proper spheroid contact. Thermal activation, then, would mean an increase in the matrix circulation and perhaps a greater acceptable angle of contact for welding. Since such a process is not diffusion controlled, but depends on probability, growth rates would behave in a systematic way, but not in accordance with any particular growth rate or activation energy.

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I. INTRODUCTION

Sintering of powder compacts in the presence of a liquid phase is an important metallurgical process since in many cases it enables the combination of materials that can not be combined by other methods, and generally results in a high-density product. During the sintering process, spheroids (usually) of the higher melting point component are surrounded by a molten matrix, and these spheroids grow if either the sintering time is increased or the temperature raised. The sintering temperatures for compositions which can be liquid-phase sintered cover an extremely wide temperature range, and numerous studies have been conducted on the kinetics of spheroid growth during the sintering operation. For example, lead-base solders are liquid-phase sintered at temperatures barely exceeding 500 K,¹ tungsten-nickel-iron composites,² tungsten-nickel-copper composites,³ and carbide-metal composites⁴ at about 1750 K, and an $\text{UO}_2\text{-Al}_2\text{O}_3$ ceramic⁵ at about 2500 K. In all of these studies, the spheroid growth rate appears to be well behaved in that the spheroid size increases with time or temperature. The generally accepted theory is that spheroid growth is controlled by dissolution of the small spheroids with simultaneous precipitation of the high melting phase from the molten matrix onto the larger spheroids, the driving force for the growth being the difference in surface energy between the smaller and larger spheroids. The slope of the log diameter-log time plot is 1/3, and should remain at this value for all liquid-phase sintered materials including ceramics, because this slope is characteristic of this spheroid growth mechanism.

Examination of published results showed a large variation in the method of presentation. Furthermore, no acknowledgment was made of solid state reactions during presintering prior to the appearance of the liquid phase, nor to the difference in size of the spheroids nucleated at the different sintering temperatures, even though each spheroid at this stage of sintering consists of hundreds of the original powder particles.

We ran a series of sintering experiments on 95% W-3.5% Ni-1.5% Fe composites and found that the slope of the log diameter-log time plot was less than 1/4. Furthermore, the activation energy for the spheroid growth process was not a single-valued

number for sintering at the various temperatures. Thus, our results show that the spheroid growth process is not governed by a single growth mechanism. These experiments were repeated using a composite which had already been liquid-phase sintered for a short time as a baseline material, and its spheroid growth rate was studied as a function of either sintering time or sintering temperature. The slopes of the log diameter-log time plots for the different sintering temperatures were not the same, and all were less than 1/4. Furthermore, the activation energies were not single-valued functions, reinforcing the viewpoint that several mechanisms were responsible for spheroid growth in this alloy composition.

II. LITERATURE APPRAISAL

The importance of understanding diffusion mechanisms during sintering was recognized many years ago, and in 1936, Mehl⁶ summarized the state of knowledge with a review of over 300 earlier papers. In 1938, Price, Smithells and Williams^{7,8} discovered the "heavy alloys" where they were able to achieve full density by liquid-phase sintering tungsten-nickel-copper at temperatures well below half of the absolute melting temperature of tungsten ($< 0.5 T_m$). They proposed that the mechanism for the growth of the essentially pure single crystal tungsten spheroids was the dissolution of the small tungsten spheroids with simultaneous precipitation of tungsten from the molten matrix onto the larger spheroids, the process being driven by the difference in surface energy between the smaller and larger spheroids. This theory is still the generally accepted one. A theory for the sintering of metal particles was proposed by Kuczynski in 1949⁹ when he found that the interface formed between two particles during sintering changed at different rates if the growth were due to either (1) viscous or plastic flow, (2) evaporation and condensation, (3) volume diffusion, or (4) surface diffusion. A theoretical treatment¹⁰ of these various diffusion mechanisms showed that the predominant mechanism responsible for particle growth during sintering under any particular set of sintering conditions could be identified. Cannon and Lenel¹¹ divided the sintering process into three phases, "liquid flow", solution and reprecipitation" and "solid phase sintering". The density of the compact increases during the liquid

flow stage, and the particles grow during the other phases. The final particle size should be limited because a very low dihedral angle is reached between two solid-liquid surfaces and the liquid phase will not permit the two particles of the solid phase to touch each other as long as the particles have different orientations. Greenwood¹² liquid-phase sintered UPb₃ in liquid lead and U in sodium, and found that the spheroid growth rate was consistent with that expected for the dissolution of the smaller spheroids with simultaneous precipitation onto the larger particles, in agreement with the earlier results of Price et. al.⁷ At about the same time, Humenik and Parikh^{13, 14} liquid-phase sintered a number of carbide-base systems. In contrast to other results, they found their results to be inconsistent with the dissolution and reprecipitation theory for spheroid growth. They advanced the "coalescence" hypothesis which attributes spheroid growth to the combination of spheroids with the rate of growth highly dependent on the surface energy relationship between solid and liquid, and the wettability of the solid phase by the liquid. Later studies by Kingery¹⁵ and King and Narasimhan¹⁶ on iron-copper composites showed that three processes were active during liquid-phase sintering. First, liquid circulation where the solid particles are rearranged. Second, the solution and reprecipitation of the solid phase, as discussed earlier, and finally, a coalescence process where the particles are so oriented that the grain boundary energy is small compared to that at the solid-liquid interface, and the material is transferred in the solid phase. Gurland¹⁷ attributed densification in cemented carbides to the same sintering mechanism. Warren and Waldron¹⁸ show that the driving force for densification in cemented carbides is a function of the surface energy of the liquid phase and is directly affected by the angle of contact of the liquid on the solid. However, there was no direct relationship between the number of contact points of the grains and the angle of contact of the liquid on the carbide. Gessinger, Fischmeister and Lukas¹⁹ attribute the rearrangement of the solid particles in the first stage of sintering to the capillary action of the liquid phase. Zukas and Eash²⁰ discount the importance of the dissolution and reprecipitation process for spheroid growth on the basis that very

Fig. 1. The effect of sintering time and temperature on the spheroid growth for an 89% W-7% Ni-4% Cu alloy. Taken from Ref. 3.

little, if any, tungsten precipitated on 500 micron diameter tungsten fibers or on W-single crystals in W-Ni-Fe composites where the remainder of the tungsten was originally present as < 2 micron diameter powder. Furthermore, capillary action of the liquid phase could help increase the density of low volume matrix composites.²¹

The spheroid growth as a function of time and temperature for 89% W-7% Ni-4% Cu taken from the work of Kothari³ (Figure 1) shows ideal experimental results for the dissolution and reprecipitation process for spheroid behavior. The log diameter-log time plots for the various temperatures have a slope very nearly equal to 1/3, in very good agreement with that predicted by theory, and the growth rates as a function of temperature are in agreement with a single-valued activation energy. The results of Sadocha and Kerr¹ for 92.3% Pb-5.2% Sb-2.5% Sn, shown in Figure 2, are also in good agreement with this theory except for specimens sintered at 518 K where the growth rate was much lower than predicted. Ceramics sintered in the presence of a liquid phase can behave in a similar way, as can be seen from the results of Lay⁵ for 99.5% UO₂-0.5% Al₂O₃ shown in Figure 3. Once again, the agreement with results predicted by the dissolution and reprecipitation theory is reasonable.

Even though there is agreement in some cases, the inconsistencies between theories and experimental results make it impossible to predict the behavior for any particular composite composition. In view

Fig. 2. The effect of sintering time and temperature on the spheroid growth for an alloy containing 92.3% Pb -5.2% Sb -2.5% Sn. Taken from Ref. 1.

of this, we studied the sintering behavior of the 95% W-3.5% Ni-1.5% Fe composite in an attempt to find out whether or not spheroid growth behavior was in agreement with the generally accepted dissolution and reprecipitation theory.

III EXPERIMENTAL TECHNIQUES

The specimens were prepared from tungsten, nickel and iron powders. Chemical analyses and powder characteristics are given in Table I. The nickel and iron powders were preblended by rolling for 8 hours at 60 rpm in bottles containing agitator wires. This blend was then added to the tungsten powder, and this mixture roll-blended in the same manner for an additional 8 hours. Being careful to prevent gravity separation, the powders were carefully packed into polyvinylchloride sacks which were then capped and sealed. Each sack was evacuated through a hypodermic needle stuck through the lid. The specimens were then placed in perforated metal holders to maintain straightness and isostatically pressed to 345 MPa (50,000 psi) without benefit of lubricants or additives. The pressed compacts were placed on alumina supports and presintered for two hours in dry hydrogen at 1673 K. The presintered specimens were machined into 0.80 cm diameter by 1.2 cm long samples, except for the special series of tests noted later, and were sintered in a self-resistance heated graphite tube furnace under a slight positive pressure of helium gas. For sintering, the specimens were supported in the center of the hot zone on a thin (0.64 cm diam.) tungsten rod, heated

Fig. 3. The effect of sintering time and temperature on the spheroid growth of a 99.5% UO_2 - Al_2O_3 ceramic. Taken from Ref. 5.

to about 1660 K, just below the presintering temperature, and allowed to equilibrate. The temperature was then raised to the sintering temperature rapidly, and zero time taken when the specimen surface reached the desired temperature. At the end of sintering, the power was cut off. Since no heat shields were used, the temperature dropped rapidly, and was generally below the presintering temperature in less than a minute.

After sintering, the specimens were sectioned, ground wet through 600 grit silicon carbide paper, dry polished on 4/0 metallographic paper, polished on 1 micron alumina, electropolished and electroetched, repolished on one micron diamond abrasive and again electropolished and electroetched. A 2% NaOH solution was used as the electrolyte. Several photomicrographs were taken of each specimen at magnifications based on spheroid size to include from 150 to 400 spheroids on each picture. Each photograph was placed under a one-matte sided transparent tracing paper, and the diameter of each spheroid measured. Each spheroid was marked after measurement so that all spheroids would be measured. For liquid-phase sintered composites, the spheroids are irregularly shaped, as can be seen from scanning electron micrographs, Figure 4, which shows zones in which at least part of the matrix is missing. Figure 4a shows the detailed shape of a few spheroids at high magnification whereas Figure 4b shows an array of spheroids of different sizes. Experimentally, such micrographs are impractical for quantitative measurements, and polished sections are used.

TABLE I
CHEMICAL ANALYSES AND POWDER CHARACTERISTICS

	W	Ni	Fe
Less than 300 ppm	Zn, Nb	--	--
Less than 100 ppm	Mo	Zn, Cd	B, Ni, Zn, Mo
Less than 40 ppm	--	Co	--
Less than 30 ppm	Ti, Zr	--	Na, K, V
Less than 20 ppm	--	K, Mo, Sn	--
Less than 10 ppm	Al, Si, K	B, V, Fe	Li, Be, Al
	V, Cr, Co	Al, Si, Ti	Cs, Ti, Cr
	Ni, Sr, Sn	Sr, Ba, Pb	Co, Cu, Sr
	Pb, Bi	Bi	Cd, Ba
Less than 4 ppm	B, Na, Ca, Mn, Fe, Cu Ag, Ba	Li, Be, Mn Cr, Na, Cu	Mg, Si, Mn
Less than 1 ppm	Li, Be, Mg	Mg, Ca, Ag	--
Bulk density (g/cm ³)	4.01	2.28	2.41
Tap density (g/cm ³)	5.84	3.68	3.66
Surface area, BET (m ² /g)	0.78	0.50	--
FSS average particle size (microns)	1.7	2.5	4.4
Median particle size, Sedibal (microns)	2.8	9.2	7.3

Figure 5a shows such a section from a specimen sintered less than a minute at 1873 K, while Figure 5b shows a similar section of a specimen given a base-line sinter and then sintered an additional 2 hours at 1963 K. The cross sections of these spheroids are not exactly circular, so each cross section is assigned a diameter (as accurately as practical) where the assigned diameter represents a circular cross section having the same cross-sectional area as the section of the spheroid being measured. Numerous studies have been made on particle size measurement²²⁻²⁵ designed to reduce the time and effort required for analysis, but these introduce a correlation factor since such measurements are seldom of the major diameter of the particle cross section visible on the polished surface. In a few cases, we tried line intercept methods of measurement, but these gave excessive scatter. The identical problem exists when a three-dimensional configuration is being described by measurements taken on a two-dimensional polished plane. This problem was recognized many years ago and was treated mathematically²⁶ for the case where the particles were perfect spheres.

For this specialized case, the average diameter of the spheres measured on a cross section was calculated to be about 79% of the true average diameter. This correction was applied to experimental data, and the results plotted in Figure 6. Note that plots for diameter, surface area and volume when using the corrected diameter give parallel lines to those for the as-measured diameters. Thus, in the usual treatment of most data, the correction need not be made since it introduces a constant multiplier. However, if one needed to know the number of powder particles in the spheroids, or some such non-linear relationship, then the correction would be necessary.

IV EXPERIMENTAL RESULTS

The experimental program consisted of two different types of experiments. First, standard sintering treatments were used so that the results for the 95% W-3.5% Ni-1.5% Fe composite could be compared with literature results on similar experiments. Secondly, a large specimen was liquid-phase sintered for a short time, and this sintered compact was then cut into specimens so that identical, well-characterized specimens could be used for the second series

Fig. 4. Scanning electron micrographs of tungsten spheroids in sintered composites. a) detailed shape of a few spheroids at high magnification, b) an array of spheroids showing size distributions.

Fig. 5. Photomicrographs of the cross-sections of two tungsten-nickel-iron composites. a) sintered for less than a minute at 1873 K, b) sintered 6.5 minutes at 1823 K followed by a 2 hour sinter at 1963 K.

of experiments. This was done to eliminate the influence of presintering treatments as well as any differences in nucleation behavior which could affect the spheroid size and growth rate during the early stages of sintering.

For the first series of experiments, presintered specimens were sintered at 1873 K for times from less than one minute to 120 minutes. The resulting average spheroid diameter is plotted as a function of sintering time in Figure 7. On the basis of the dissolution and reprecipitation mechanism for

spheroid growth, the slope of the plot should be $1/3$, whereas it is actually closer to $1/4.3$. This indicates either very fast spheroid growth at short times, or that the spheroids during the initiation of liquid-phase sintering were already of considerable size, either because of reactions during the presintering treatment or because of some unexpected nucleation phenomena. The spheroid size distribution for the various sintering times is shown in Figure 8. The distribution is consistent in that with increasing sintering time, the number of small

Fig. 6. Differences in diameters, surface areas and volumes for spheroids measured on a sectioned surface compared to the calculated values for these same spheroids where the true diameter is determined from a three-dimensional plot.

Fig. 7. Spheroid growth as a function of sintering time for 95% W-3.5% Ni-1.5% Fe sintered at 1873 K.

spheroids decrease and a few larger ones are grown. Obviously, if the average spheroid size increases, the number of spheroids in a given volume must decrease. This spheroid diameter distribution as normalized is shown in Figure 9. Again, this points out that the number of small spheroids decreases and the number of large ones increases, and even larger ones are grown as the sintering time increases. If the growth process were entirely by dissolution of the small spheroids with simultaneous reprecipitation of tungsten from the molten matrix, then one should expect to find some inconsistency in this

Fig. 8. Spheroid size distribution as a function of sintering time for a constant cross-sectional area. Not normalized.

relationship, because at the longer times, more and more smaller spheroids would have to be dissolving to sustain the required growth of the larger spheroids. To examine this aspect more closely, the size distributions for each sintering time were divided into five equal fractions, and the average spheroid diameter for each fraction determined. These are plotted in Figure 10. Note that all fractions grow at about the same relative rate. Since several small spheroids must decrease in size to sustain the growth rate of a single large spheroid, we would expect some inconsistency in the growth rate of at least one of the smaller size fractions, but none is found. Again, this is not in agreement with the generally accepted dissolution and reprecipitation mechanism for spheroid growth.

A number of additional sintering experiments were conducted on the presintered composites at different sintering temperatures so that the activation energy for growth could be determined. The

Fig. 9. Spheroid size distribution as a function of sintering time for the same composite shown in Figure 8. Normalized.

Fig. 10. Spheroid growth as a function of time for 20% increments of spheroid size for the 95% W-3.5% Ni-1.5% Fe composite sintered at 1873 K.

Fig. 11. Spheroid size distribution as a function of sintering temperature for the composite sintered for 120 minutes.

spheroid size distributions for experiments at three different temperatures for a time of 120 minutes are shown in Figure 11. Again, note that the number of small spheroids decreases as the number of large ones increases with increasing sintering temperature. Since the growth process is thermally activated, the activation energies for different temperature intervals should be the same if a single process is rate controlling for spheroid growth. Since the log diameter-log time plots are straight lines of slope n , the spheroid diameter, D , can be related to time, t , by

$$D = K_o t^n \quad (1)$$

where K_o is a temperature dependent rate. Since K_o expresses the rate at which the average spheroid size increases, it can be related to temperature by

$$K_o = A e^{-Q/RT} \quad (2)$$

where Q is the activation energy, R the gas constant, T the absolute temperature and where A is a reaction constant. A plot of $\log K_o$ vs $1/T$ for tests run at different temperatures will be a straight line if a single growth process is controlling. The slope of this line will give the activation energy for the growth process. Methods for determining the activation energies for creep processes have been

TABLE II

ACTIVATION ENERGIES FOR 95% W -3.5% Ni -1.5% Fe SINTERED 120 MINUTES

Temperature Range, K	Spheroid Diameters** microns	Activation Energy kcal/mole	Activation* Energy kcal/mole
1733 - 1873	23.31 - 31.88	43.2	68.6
1873 - 1963	31.88 - 34.41	18.6	26.6
1733 - 1963	23.31 - 34.41	34.3	53.4

* Assuming a nucleation size of 10 microns which was subtracted from all final spheroid diameters.

** Generally, particle diameters were estimated to the nearest micron, and these numbers are averages of several hundred particles used strictly for calculational purposes.

described by Dorn²⁷ and for nucleus growth by Byrne.²⁸ Since A, R and Q will be the same for a single spheroid growth process at two different temperatures, we can calculate the activation energy for the process by relating the growth in the same time period as follows:

$$Q = \frac{RT_1 T_2}{T_2 - T_1} (\ln D_2 - \ln D_1) \quad (3)$$

where D_2 is the spheroid diameter at the higher temperature T_2 and D_1 is the spheroid diameter at temperature T_1 . Since activation energies calculated from equation 3 are inconsistent with other data available, it was felt that the growth was really a volume function rather than one simply of diameter, and that equation 3 should be modified in the following manner:

$$Q = \frac{RT_1 T_2}{T_2 - T_1} (\ln kD_2^3 - \ln kD_1^3) \quad (4)$$

which gives

$$Q = \frac{RT_1 T_2}{T_2 - T_1} (3 \ln D_2/D_1). \quad (5)$$

Referring back to Figure 11, the activation energies for the runs are shown in Table II. In addition to the measured diameters, calculations were also made where it was assumed that the nucleation size of the spheroids was 10 microns, and this was subtracted from the final diameters (the assumption

was based on the grain sizes of presintered compacts). The scatter in the activation energy values indicates that either the process of spheroid growth is not a continuous function of temperature, or that more than one growth mechanism is operating.

There are several questionable aspects of the experiments already described, and to those done by other experimentalists studying the behavior of the liquid-phase sintering process. For one thing, the effect of solid-state sintering reactions on nucleation behavior is completely ignored for tests run at different temperatures. Evidently, the assumption is made that the spheroids formed initially have equivalent diameters and size distributions. Secondly, it is assumed that the structures after a specified sintering time at different sintering temperatures are equivalent, even though the diameters, surface areas and volumes are different. Since the generally accepted theory of dissolution and reprecipitation derives its motivation from surface energy based on particle size differences, matrix pockets are different in both size and shape for different size spheroids, and other variables are present, the structures which are compared do not appear to be equivalent.

To circumvent the aforementioned difficulties, a different set of experiments were conducted. First, a long rod of the presintered composite was liquid-phase sintered for 6.5 minutes at 1823 °, and this sintered composite was cut into small specimens which were used as the baseline material for the succeeding experiments. Then, activation

Fig. 12. Spheroid growth as a function of sintering time for the composite which had been given a baseline sinter for 6.5 minutes at 1823 K.

Fig. 14. Spheroid size distribution of the baseline sintered composite after additional sintering at 1963 K.

Fig. 13. Spheroid size distribution of the baseline sintered composite after additional sintering at 1873 K.

energies were based on the times required at the different temperatures to achieve the same structures. Hopefully, comparisons would be made on sintered specimens having the same size spheroids (same diameter, same surface area and same volume), matrix pockets of similar size and shape, same spheroid size distribution, and all other structural variables the same. The activation energy could then be calculated by:

$$Q = \frac{RT_1 T_2}{T_2 - T_1} (\ln t_2 / t_1), \quad (6)$$

where t_2 is the time required at temperature T_2 to achieve the same structure as that obtained by time t_1 at temperature T_1 . Plots of spheroid growth as a function of sintering time for various sintering temperatures are shown in Figure 12. The spheroid size distribution for specimens sintered either an additional 3 minutes or 120 minutes at 1873 K is shown in Figure 13. Similar plots for a number of sintering times at 1963 K are shown in Figure 14. Note that the sintering behavior was consistent with earlier experiments in that the number of small spheroids decreased, and larger spheroids were formed for the longer sintering times. The divergence of the plots of average spheroid diameter with sintering time for the various sintering temperatures shows that the spheroid growth process can not be described by a single activation energy. To demonstrate that identical structures are being compared, the spheroid size and spheroid size distribution of specimens sintered for 40 minutes at 1963 K are shown with those from a specimen sintered for 120 minutes at 1873 K in Figure 15. The structures of these two composites are essentially the same. The calculated activation energy is 89.2 kcal/mole. This is much higher than the 66.6 kcal/mole calculated for

Fig. 15. Comparison of average diameter and spheroid size distributions for the baseline composite sintered for different times and different temperatures to achieve similar structures.

the different size spheroids after a constant sintering time of 120 minutes. Calculations by either method for other times to reach an equivalent size, or for different sizes at constant sintering times give different activation energies.

V DISCUSSION

Producing materials by liquid-phase sintering is of widespread interest since such a process can be used for some materials at temperatures at least as low as 518 K, and has been used for ceramics at temperatures approaching 2500 K. All of these materials behave similarly in that a solid phase exists in a liquid matrix during sintering. This solid phase usually consists of spheroids which increase in size in a systematic manner if either the sintering temperature or the sintering time is increased. Since the spheroid size and size distribution affect the final properties of the composite, it is important to understand the spheroid growth process. An early theory for growth⁷ proposed a mechanism whereby small spheroids dissolved while simultaneously, material precipitated from the melt onto the larger particles, the growth process being driven by the difference in surface energy between the smaller and larger spheroids. Although this mechanism is still generally accepted, there are experimental results which are not completely in agreement with such a theory.¹⁵⁻²¹

Specimens of 95% W-3.5% Ni -1.5% Fe were liquid-phase sintered in the usual manner and we found that the slope of the log diameter-log time plot was much less than the 1/3 predicted by the dissolution and reprecipitation theory. Furthermore, tests run at different sintering temperatures were not consistent with a single-valued activation energy. Therefore, our results were not consistent with such a theory.

Furthermore, the results of our earlier tests as well as the results from those reported in the literature are of questionable value because the materials sintered at different temperatures may have been different at the initiation of the liquid-phase sintering process. Any effects from presintering or of nucleation size were ignored. Also, most results compared spheroid sizes after a specified sintering time. Thus, large diameter spheroids having low surface energies were compared with small diameter spheroids having high surface energies. Furthermore, other structural features, such as matrix pocket size and shape, distance between spheroids, etc., were different. These objections were satisfied by starting the second portion of the experimental program with composites which had been liquid-phase sintered for 6.5 minutes and had well-formed spheroids whose average diameters were just slightly larger than 13 microns. Thus, additional sintering would simply cause these spheroids to grow. Spurious effects from solid state presintering, size of spheroids after nucleation at the different sintering temperatures, and other variables were eliminated. Furthermore, activation energies were determined by comparing the times necessary to achieve a similar average spheroid diameter and spheroid size distribution thereby eliminating differences in distance that the tungsten would have to migrate to reach a deposition site, as well as other structural variables. We compared equivalent structures.

Results from this experimental program showed that the slope of the log diameter-log time plot was considerably less than 1/3 indicating that the growth mechanism was not solely that of dissolution of the small spheroids with simultaneous precipitation of tungsten from the molten matrix onto the larger spheroids. This is not to imply that such a growth process does not take place simultaneously with some other mechanism. Also, the

Fig. 16. Spheroid size distributions for the baseline alloy, and to show the change in size distribution if two like particles combined in a unit of time. This hypothetical case is to be compared with experimental data obtained at 1963 K in Figure 14.

log diameter-log time plots for sintering at different temperatures are not parallel, showing that the spheroid growth process is not controlled by a single growth mechanism. Activation energies calculated on the basis of time required to obtain an equivalent structure vary over a wide range depending on the choice of spheroid diameter used in the calculation. Again, this points out that the growth process is not controlled by a single growth mechanism, or that the mechanism is not well-behaved with regard to thermal activation. Such a mechanism could be "coalescence", as suggested for the third stage of growth.¹³⁻¹⁸ The process could be described as the movement of the spheroids aided perhaps by capillary forces until contact with another spheroid having a similar crystallographic orientation. Welding would take place and the boundary formed (equivalent to grain boundary) would migrate until it reached the "new" spheroid surface. This would be a requirement since the spheroids are essentially pure tungsten single crystals. This boundary motion is not unreasonable since we know that grain boundaries can move in pure tungsten at temperatures well below the liquid-phase sintering temperature.²⁰ Since the "new" spheroid is surrounded by the liquid matrix, the surface tension forces would tend to make the new mass spherical.

The growth then would be a function of the probability with which spheroids of similar orientations come into contact with one another. It is possible to predict the spheroid size distribution after various times for the coalescence mechanism for spheroid growth if the size distribution is known at some prior stage since the combination of two or more spheroids would depend on the probability for touching when properly oriented, which in turn is dependent on the number of each size present. To determine whether or not such a study is worthwhile, we made a simplified assumption that during each time increment, two spheroids of equal size combined. By adding the volumes for each spheroid, the new volume is obtained, and from this, the diameter of the new spheroid calculated. One can then determine the spheroid size distribution of the new spheroids. We did this exercise for four successive combinations for the compact used as the baseline material for the experimental particle growth studies. The results are shown in Figure 16. Figure 16 can be compared to measured spheroid size distributions for this same baseline material after sintering experiments at 1963 K for various times shown in Figure 14. The two figures are similar in many respects, even though the calculated distributions do not allow for any spheroid to become smaller by dissolution.

The effect of presintering and the nucleation of spheroids during the initiation of liquid-phase sintering has not been studied in any detail. Most studies tend to ignore the first few minutes of sintering (for example, no reliable data could be obtained during the first ten minutes in the study of solders, reference 1), and as a consequence, the results are based on a comparison of the behavior during additional sintering of two different starting materials. No one has proposed the coalescing of particles during the early stages of sintering. If we calculate the growth of particles by the use of equation 10 from Greenwood,¹² the calculated growth rate is much too slow to account for experimental observations. On this basis, we propose that coalescence is important in spheroid growth during all stages of the sintering process. Perhaps solid state diffusion is important since some 200 powder particles were needed to form the first resolvable spheroids we observed after less than a minute of

liquid-phase sintering time. The volumes of these spheroids increased by more than 2-1/2 times during 5 minutes additional sintering at 1873 K. Such growth rates appear incompatible with a dissolution and reprecipitation process.

VI CONCLUSIONS

The slopes of the log diameter-log time plots describing the growth of spheroids during the liquid-phase sintering of presintered 95% W-3.5% Ni-1.5% Fe composites were less than 1/3 and their activation energies on sintering at different temperatures were not a single value. Furthermore, similar experiments where the baseline material had already been liquid-phase sintered to where the individual spheroids were resolvable gave similar results. Thus, either the spheroid growth process is not controlled by a single growth mechanism, or the mechanism, although thermally activated, does not depend on temperature in a systematic way. Coalescence of spheroids has been proposed as a third stage of sintering, after particle rearrangement followed by dissolution and reprecipitation of the solid phase. Because of the spheroid growth rates in this composite composition, much faster than proposed in the present theories, we propose that the spheroids coalesce when contact is made between spheroids of similar orientations, and that this process occurs throughout the liquid-phase sintering cycle. Undoubtedly, dissolution of the small spheroids and reprecipitation of tungsten from the molten matrix onto the larger spheroids occurs simultaneously, but the spheroid growth from this process is slow.

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