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**Experimental Evidence for Several Spheroid Growth
Mechanisms in the Liquid-Phase
Sintered Tungsten-Base Composites**

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EXPERIMENTAL EVIDENCE FOR SEVERAL SPHEROID GROWTH MECHANISMS IN THE LIQUID-PHASE SINTERED W-BASE COMPOSITES

by

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ABSTRACT

The generally accepted mechanism for spheroid growth during sintering of tungsten-base composites in the presence of a liquid phase is the dissolution of the small 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 larger and smaller spheroids. From theoretical considerations, the slope of the straight line of log diameter versus log time should be $1/3$ for this process. The experimental evidence for the dissolution and reprecipitation mechanism is meager, being based primarily on the spheroid growth rate during the latter stages of liquid-phase sintering. We present experimental evidence that shows spheroid growth taking place in systems where the tungsten and the matrix are mutually insoluble thereby making dissolution and reprecipitation impossible. Furthermore, the results from these studies and others using the usual matrix compositions indicate that spheroid growth takes place predominantly by the combination or coalescence of two or more spheroids. Deposition of tungsten from the molten matrix also occurs, although not necessarily on spheroid surfaces which have the lowest surface energy. Thus, many mechanisms, each depending on temperature and other variables, operate simultaneously. A satisfactory theoretical treatment must include them all.

I. INTRODUCTION

When W-rich W-Ni-Fe composites are sintered in the presence of a liquid-phase, the tungsten spheroids grow with time of sintering, and the growth rate increases as the sintering temperature is increased. The generally accepted mechanism for spheroid growth is the dissolution of the smaller sized spheroids with simultaneous precipitation of W from the melt onto the larger sized spheroids. The driving force for such a process is the difference in surface energy between the small

and large spheroids. There is some opposition to this theory, however, with coalescence of the spheroids being proposed as an alternative growth mechanism.

All of the previously proposed growth mechanisms lack experimental verification. We propose that spheroid growth is not governed by a single mechanism, but by two or more mechanisms operating simultaneously. Furthermore, dissolution and reprecipitation is not the dominant growth mechanism. These conclusions are supported by

experimental results.

II. BACKGROUND

In 1938, Price, Smithells and Williams^{1, 2} discovered the "heavy alloys" during their search for a tungsten alloy to be used in radiation shielding. Their alloys were mainly tungsten with small amounts of copper and nickel. During sintering in the presence of a liquid phase, the original fine tungsten particles disappeared and were replaced by fairly uniform spheroids with diameters about 30 times those of the original particles. They proposed a mechanism of solution of the small particles with simultaneous precipitation of tungsten from the matrix which is supersaturated with respect to the larger spheroids. When they sintered compacts made from coarse W powder containing few particles less than 1 μm in the presence of a liquid-phase, very little spheroid growth took place. They stated that as soon as all the small particles dissolved there was no longer a large difference in solubility, which is essential to growth. As further proof, they pointed out that in the liquid-phase sintering of tungsten in pure copper, there was practically no change in the size of the tungsten particles and no reduction in porosity. They attributed this to the mutual insolubility between W and Cu.

In 1949, Kuczynski published a theory for the sintering of metal particles.³ He found that the interface formed between two particles during sintering changed at different rates depending on the growth mechanism. The growth mechanisms were divided into 1) viscous or plastic flow, 2) evaporation and condensation, 3) volume diffusion, and 4) surface diffusion. A theoretical treatment of these various diffusion mechanisms by Herring⁴ showed that the predominant mechanism of particle growth during sintering could be identified. Cannon and Lenel⁵ were in general agreement with the dissolution and precipitation theory but felt that it had to be extended in two areas. They found that, under suitable conditions, rapid densification

occurred even if the solubility of the solid phase in liquid was negligible. They attributed the first stage of densification to a "liquid flow" mechanism in which the liquid carrying solid particles in suspension flows into the pores of the compact. They proposed that this was the case even for systems in which there was considerable solubility. They also proposed a cessation of densification which they attributed to the formation of a rigid skeleton of solid phase caused by a positive dihedral angle between two grains of the solid phase and the liquid phase. Growth of the spheroids could continue by solution and reprecipitation even after densification stopped. Here, the dihedral angle refers specifically to the angle the liquid phase makes at the boundary of two grains of solid phase. Mathematically, a zero dihedral angle means that two solid-liquid interfaces can be maintained at a lower energy than one solid-solid interface (grain-boundary). Therefore, the liquid phase will not permit two spheroids with different orientations to touch each other, but will keep such particles separated. Kingery⁶ and Kingery and Narasimhan⁷ found that sintering of iron-copper gave similar results to those of Cannon and Lenel in that there were three distinct phases of sintering. First, liquid circulation where the solid particles are rearranged, followed by the dissolution and reprecipitation process and then coalescence where material is transferred in the solid phase. In a study of cemented carbides,⁸ Gurland attributed densification to the same sintering mechanisms with the stipulation that coalescence is impossible during the first two sintering stages. Warren⁹ studied the spheroid growth behavior during liquid-phase sintering of VC-Co and his results support the dissolution and reprecipitation theory. He studied the contiguity of the VC spheroids, which he defined as the average fraction of the surface area shared by one spheroid with all of its neighboring spheroids. The contiguity fell very rapidly from lots of contact at the beginning of sintering to a low constant

contact value as sintering progressed. This is consistent with the concept of an equilibrium value of contact controlled by the ratio of the interfacial energy to the contiguous boundary energy. However, there was no direct relationship between the contiguity and the angle of contact of the liquid on the carbide. The initial degree of contact or contiguity varies quite a bit depending on presintering conditions, and the extent to which contiguity increases or decreases during subsequent liquid-phase sintering depends not only on the equilibrium degree of contact but also on presintering history. Arguments were presented to show that this behavior was not inconsistent with the generally accepted dissolution and reprecipitation spheroid growth theory. This study was expanded by Warren and Waldron,¹⁰ and their conclusions reinforced those of the earlier study.

The results from a number of experimental programs support the dissolution and reprecipitation theory for spheroid growth. For example, Greenwood¹¹ liquid-phase sintered UPb_3 in liquid lead, and uranium in liquid sodium. The spheroid sizes were quite small, and the growth times long, but the growth rate was consistent with that expected based on this growth theory. That is, that $\log D$ (spheroid diameter) vs $\log t$ (time) has a slope equal to $1/3$ for a single sintering temperature, and that results from specimens sintered at different temperatures would have a single-valued activation energy. Kothari¹² studied a number of composites very similar to ours, and his results also agreed with the dissolution and reprecipitation theory. Some of his results from the 89% W-7% Ni-4% Cu composite are shown in Fig. 1. The slopes of $\log D$ vs $\log t$ are all about $1/3.2$, and results from experiments at different temperatures can be represented quite nicely by a single-valued activation energy. Other composites exist which must be sintered over quite different temperature ranges, showing that spheroid growth is an important variable in a large number of liquid-phase

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. 12.

sintered composites. For example, Sadocha and Kerr¹³ studied Pb-Sb-Sn and Pb-Sb-Sn-As solders where they used sintering temperatures only slightly greater than 500 K. Their spheroid growth rates for 92.3% Pb-5.2% Sb-2.5% Sn at a number of different temperatures from 518 K to 533 K are shown in Fig. 2.

Their results agree favorably with the dissolution and reprecipitation theory except for specimens sintered at 518 K where the growth rate was too low. At short times, below 10

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. 13.

minutes, they could not get reproducible measurements for spheroid diameter for any of their tests, thus limiting their analyses to times of 10 minutes and longer. Even ceramics sintered in the presence of a liquid-phase behave in a similar way. The results of Lay¹⁴ for 99.5% UC_2 -0.5% Al_2O_3 sintered at temperatures from 2273 K to 2473 K are shown in Fig. 3. The slopes of $\log D$ vs $\log$ sintering time (t) vary from 1/2.5 to 1/3.1, which is in reasonable agreement with a slope of 1/3, the slope which one should get if the controlling growth mechanism is dissolution and reprecipitation.

The results from a number of other liquid-phase sintering experiments were not in agreement with the dissolution and reprecipitation mechanism for spheroid growth. For example, Blumenthal and Silverman¹⁵ found excessive growth of TiC particles in the TiC-Ni system after only 5 minutes sintering and their size did not increase significantly with longer sintering times. Humenik and Parikh^{16,17} studied a number of liquid-phase sintered carbide-base systems. Of particular interest were their studies of the WC-Co and WC-Cu systems. For the WC-Co system, there is a large solubility of WC in cobalt, but WC is practically insoluble in copper. Thus, if spheroid growth is controlled by the dissolution and reprecipitation theory, one should expect to get large particles in liquid-phase sintering

the WC-Co composites, and small particles in the WC-Cu system. The experimental results were exactly opposite with large particles in the WC-Cu system and small particles in the WC-Co system. To explain this behavior, 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. Krock^{18,19} believes that spheroid growth in the W-base composites results from the agglomeration of solid W-particles in the liquid phase which then combine with existing spheroids as evidenced by the marked frequency of peaks at regular intervals in the particle size distribution; and that this is followed by continued spheroid growth by volume diffusion. Also, with identical sintering times and temperatures, the average spheroid size increased as the amount of liquid matrix decreased.

Gessinger, Fischmeister, and Lukas²⁰ attribute densification during the early stages of sintering to rearrangement of solid particles by capillary action of the liquid. Since the average distance between particles at this stage of sintering is small, movement of the molten matrix can take place, and this appears to be the reason for achieving essentially theoretical densities in low volume matrix W-Ni-Fe composites.^{21,22} In an experiment designed to test the dissolution and reprecipitation theory, Zukas and Eash²³ substituted 500- μm -diameter W-fibers for part of the 2- μm -diameter powder in liquid-phase sintered W-Ni-Fe compacts. For fibers which had been given a prior recrystallization anneal, little if any W deposited on their surfaces. The fibers which were left in the cold-worked condition after drawing were completely dissolved by the matrix. Thus, factors other than surface energy are important and cannot be ignored.

Studies on the sintering behavior of liquid-phase sintered W-Ni-Fe composites by Zukas and

Fig. 3. The effect of sintering time and temperature on the spheroid growth of a 99.5% UC_2 - Al_2O_3 ceramic. Taken from Ref. 14.

Sheinberg^{24, 25} gave additional evidence that the dominant spheroid growth mechanism was not dissolution and reprecipitation of W. If it were, then during the growth process, more and more small spheroids would have to grow smaller to feed just a few larger ones. Under these conditions, one would expect a shift in the particle size distribution. No such shift occurs, as can be seen from a plot of size fractions of spheroids versus sintering time in Fig. 4. Another set of experiments was designed to eliminate material differences in test specimens due to different presintering conditions, so that the only variable would be sintering temperature. A long rod of the presintered composite was given a liquid-phase baseline sinter of 6.5 minutes at 1823 K, which was sufficient to produce small well-formed spheroids. This liquid-phase sintered control rod was then cut into several pieces, each of which was then sintered for an additional time at one of three other sintering temperatures. The resulting spheroid size as a function of sintering time is shown in Fig. 5. There are several important points which are evident from this figure. First, all of the lines have slopes much lower than 1/3, the slope that one should get for the dissolution and reprecipitation growth mechanism according to the theories advanced so far. Second, the plot for each

Fig. 4. 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. 5. Spheroid growth as a function of sintering time for the composite which had been given a baseline sinter for 6.5 minutes at 1832 K.

temperature is a straight line. There is no transient period where the growth rate tries to adjust for the different sintering temperatures indicating that presintering conditions do affect the later results. Third, the temperature effect on the growth process cannot be described by a single-valued activation energy. An example of the effect of sintering temperature on structure is shown in Fig. 6. Figure 6a shows the presintered structure of a 95% W-3.5% Ni-1.5% Fe composite sintered about 40 K below the matrix melting point. The white areas are patches of Ni-Fe. Figure 6b shows the structure at about 20 K below, and 6c at approximately the matrix melting temperature. As soon as the matrix becomes molten, the particles tend to become spheroids, but large patches of matrix are still present. Figure 6d shows the structure at about 20 K above the matrix melting temperature where the spheroids are nicely formed and the matrix is fairly uniformly distributed. The size of the W spheroids formed at the beginning of liquid-phase sintering appears to be directly related to the presintered grain size. Figure 7 shows a similar series of structures of the same specimen at different distances from the hot zone for a specimen sintered in a temperature gradient. Note

Fig. 6. Effect of presintering temperature on composite structure. In order of increasing temperature, a to d.

that the particles grow with decreasing distance from the hot zone (7a to 7d) and become spheroidal shortly after the matrix becomes molten. The dislocation etch pits suggest that the particles have considerable internal energy, perhaps because of the stresses imposed by interaction during the solid state presintering operation and thermal stresses generated by differences in expansion. Thus, either the growth process is not a regular function of temperature, or as is more likely the case, there are several growth mechanisms operating simultaneously where the predominant mechanism changes in response to changes in the sintering conditions.

III. EXPERIMENTS AND RESULTS

The results from a number of diverse experiments form the basis for this report. Therefore, each set of experiments will be discussed individually with regard to the techniques and results. The typical structure of such composites after liquid-phase sintering consists of single crystal tungsten spheroids which are body-centered-cubic embedded in a ductile face-centered-cubic W-Ni-Fe matrix. The general appearance is shown in Fig. 8. Figure 8a is of a fractured surface encompassing a matrix deficient pore. Note the "river" patterns on the cleaved spheroids

Fig. 7. Effect of distance from the hot zone (or temperature) on the structure of the same specimen of 95% W-3.5% Ni-1.5% Fe. In order of decreasing distance from the hot zone, a to d.

Fig. 8. Typical composite structures: a) fractured surface encompassing a matrix deficient area showing shape and size distributions of spheroids in composites as well as fractured spheroids, and b) an enlarged view of a few spheroids.

which are typical for W-single crystals.^{26, 27}

Figure 8b shows the detailed shapes of a few spheroids. The following experiments are related to the way in which these spheroids behave during liquid-phase sintering.

A. Effect of Cold Work Introduced by Mechanical Pressing

If a sintered W-base composite having some porosity is reheated to the original sintering temperature, there is little tendency for the matrix to fill the pores even though there is considerable movement of the matrix, Fig. 9a. Pressing the composite about 25-30% induces energy into both the spheroids and the matrix. Resintering at

1693 K, below the melting point of the matrix, is sufficient to recrystallize the W-spheroids, but matrix movement in the solid state is slow and the pores remain unfilled, Fig. 9b. However, by increasing the sintering temperature to 1753 K where the matrix is molten, the matrix fills the pores and the recrystallized grains become new spheroids, Figs. 9c and 9d. The effect of cold work on the recrystallization and grain boundary attack can be seen much better if a composite of larger average spheroid size is used for the experiments, Fig. 10. Figure 10a shows the structure of a composite pressed to a 30% reduction at room temperature. Figures 10b and 10c show new spheroids which have

Fig. 9. Tungsten base composite: a) as resintered, pores are not filled by the matrix, b) pressed 30% and held at 1695 K where the matrix is still solid [W-spheroids recrystallize but pores remain unchanged], c) pressed 30% and resintered at 1753 K [recrystallized grains form new spheroids and matrix fills pores], and d) same as c except at higher magnification.

Fig. 10. Effect of cold work on a sintered composite, and its behavior during additional liquid-phase sintering: a) pressed 30%, b) a +2 minutes at 1825 K, c) a +2 minutes at 1825 K, and d) a +6 minutes at 1750 K.

formed from the small recrystallized surface grains, but coalescence begins before the old spheroids are completely divided, and spheroid growth continues, Fig. 10d. The process can be seen in better detail at higher magnification, Fig. 11. Figure 11a shows the pressed structure, and Figs. 11b through 11d show this structure after resintering. Note the grain boundary attack, small spheroids clinging to the large ones, and the presence of a few new small spheroids completely isolated from the large ones. Additional sintering promotes coalescence, Fig. 12a, and a trend back toward sphericity, Fig. 12b. Longer sintering times should make them more spherical since the

energy from pressing has now been dissipated and surface tension forces are acting on particles completely surrounded by liquid matrix at temperatures where diffusion in the solid state takes place readily.

B. Tungsten Deposited in Cracks and Grain Boundaries of Fibers

An earlier study²³ showed that as-drawn W-fibers were completely dissolved when liquid-phase sintered with W-Ni-Fe because of their high energy content, while the low energy recrystallized fibers were not attacked. Furthermore, little if any tungsten from the W-saturated matrix deposited on the fiber surfaces, indicating that the dissolution and reprecipitation mechanism for

Fig. 11. Similar to Fig. 10 except at higher magnification: a) pressed 30%, and b-d) a +2 minutes at 1825 K.

Fig. 12. Sintered compacts pressed 30% given an additional sintering treatment: a) 6 minutes at 1825 K, and b) 30 minutes at 1975 K.

spheroid growth was probably not the predominant growth mechanism in this system. Additional experiments with recrystallized fibers which were either cracked during their preparation or those whose grain boundaries were attacked during the liquid-phase sintering process support the conclusion that other growth mechanisms are predominant. In one instance, Fig. 13a, about 25 μm of W has deposited on the fiber surface, as well as on grain boundaries to distances greater than 160 μm from the surface. Other fibers, Fig. 13b, had W deposited on small crack surfaces but not on the larger cracks. The deposition of W in these cases does not appear to be governed by surface energy considerations.

C. Spheroid Nucleation from the Molten Matrix

If one assumed that spheroid growth was governed solely by the dissolution and reprecipitation theory where W dissolved from the higher energy sites and deposited on those of lower energy, then one could control, or even select, the growth sites by overwhelming the surface energy differences between large and small spheroids with energy supplied through an external source. A variation of zone melting, i.e., directional solidification, appears ideally suited for this purpose. One could

merely set the presintered compact on a W-pedestal, apply heat over a fairly narrow zone with the hot zone centered at the compact-pedestal junction, increase the temperature to that normally used during sintering, and then slowly raise the hot zone. A solid-liquid junction will exist at some set distance both above and below the hot part of the zone, and these should be areas of minimum energy in the zone. Since the hot zone moves upward, the upper minimum energy area will change position with the former zone increasing in energy during the experiment, while the lower one will solidify and remain solid. Thus, W from the supersaturated molten matrix should deposit on the pedestal, and the W-crystal or crystals grow upward as the hot zone is slowly raised.

When we tried this experiment using standard presintered specimens, we obtained the usual sintered compact having the typical spheroids embedded in the matrix-structure setting on the W-pedestal. The results were inexplicable, and so the experimental procedure was revised. It was decided to use specimens which had already been liquid-phase sintered so that effects from different presintering treatments could be ruled out and only the change in structure caused by additional

Fig. 13. Cross sections of 500- μm W-fibers: a) W deposited on fiber surface and on internal grain boundaries, and b) W deposited on small crack surfaces in a W-fiber but not on the surfaces of all of the large cracks.

liquid-phase sintering could be studied. Also, to simplify the interpretation of the results, a tapered gap ($\sim 2^\circ$) between the W-pedestal and the sintered compact was introduced by using an annealed W-wire of the proper diameter as a wedge on one side of the pedestal to insure the proper separation. Thus, the molten matrix supersaturated in W would fill the gap, deposit its excess W, and circulate for a refill. The change in structure along the gap would give information about the effect of distance between spheroids thereby enabling us to choose the proper zone speed for directional growth during sintering. The zone speed was controlled by raising the specimen by means of a feed screw connected to a constant speed motor through a gearbox. Speeds from 0.1 mm to 25 mm per minute were used. A heavy-walled graphite tube heater with a 3-mm slot gave a uniform hot zone slightly greater than 2 mm. A slight positive pressure of helium was used to protect the composite and to keep vaporization of the molten matrix at a minimum.

Figure 14a shows a typical structure of the composite-pedestal interface. Tungsten from the melt deposited on the pedestal with what appears to be a preferred-orientation pattern. The deposited W had a height about equal to twice the average spheroid diameter, and this was about as much preferential growth of W as we were ever able to get. Figures 14b and 14c show the effect of a slightly wider gap. The use of single crystal W-pedestals changed the gap appearance slightly but the column height of deposited W did not increase noticeably. There were W deposits on some of the spheroids and new globs of W which had been nucleated but were not spheroidal in shape, Fig. 14d. Closer examination showed that a large number of new particles were nucleated, Figs. 15a through 15d, some spheroidal and many not. For most of these, a very slow zone speed was used (0.25 mm/minute). It is interesting to note that a large number of these new spheroids formed almost adjacent to the original spheroids. This appears to

be very much in disagreement with the dissolution and reprecipitation theory for spheroid growth since the concentration of W in the matrix should be less than average near the larger than average spheroids where W is depositing preferentially.

A similar experiment was done in which two pieces of presintered composite were sintered with a tapered gap between them for the purpose of getting a matrix pocket large enough for chemical analysis with the microprobe. After sintering there were no large matrix pockets; there wasn't even any demarcation at the joint. Determining the position of the junction was possible only because of a slight surface offset of the two pieces at the junction because of misalignment during the positioning before sintering. The experiment was repeated using specimens which had already been liquid-phase sintered. After resintering, the gap was filled by small-sized spheroids, Figs. 16a and 16b, which must have nucleated in the matrix since they were smaller than most of the spheroids present at the beginning of the second sintering treatment. Again, such spheroid nucleation and growth behavior is not in agreement with the dissolution and reprecipitation theory.

D. SEM Analysis of Fracture Composite Surfaces

At room temperature and below, composites fail chiefly by cleavage through the single crystal tungsten spheroids. Many such fractures were examined with the scanning electron microscope (SEM). In many cases, there were pockets of a ductile material completely surrounded by tungsten, and exposed only after cleavage of the W-spheroids. Figures 17a-d show such pockets of ductile material on cleavage planes which were flat. Many of these pockets were analyzed with the SEM and were found to be the same composition as the matrix material, within the analytical accuracy of the SEM. Many of the larger matrix pockets completely surrounded by pure tungsten approach 10 μ m in diameter. It is

Fig. 14. Composite-tungsten pedestal interface for zone sintering experiments: a) columnar crystal of W deposited from the matrix on tungsten, b) matrix patch at interface, c) matrix patch at interface, and d) nucleation of new particles in matrix.

Fig. 15. a-d) Nucleation of new spheroids and particles in matrix at W-pedestal-composite junction.

Fig. 16. a, b) New spheroids formed during sintering in a tapered gap between two pieces of composite which had already been liquid-phase sintered.

Fig. 17. a-d) Matrix pockets completely surrounded by tungsten observed by SEM after cleavage of the W-spheroids.

inconceivable that such matrix pockets could be formed if the only growth process was by precipitation of W from the molten matrix.

E. Liquid-Phase Sintering of Tungsten in Either a Copper or Gold Matrix

The spheroid growth process based on dissolution of the small spheroids and reprecipitation of the high melting phase from the liquid onto the lower surface energy larger spheroids requires that the solid or high melting phase be soluble to an appreciable extent in the molten matrix. Because W is essentially insoluble in either Cu or Au, there should be no spheroid growth during the liquid-phase sintering process in either the W-Cu or W-Au systems. Price *et al.*¹ reported that they

found practically no change in the size of the tungsten particles and no reduction in porosity when they liquid-phase sintered W with Cu. Cannon and Lenel⁵ reported that they observed a slight amount of particle growth after 6-hours sintering along with an increase in density. Such contradictory results cloud the issue as to whether other spheroid growth mechanisms are operative.

For our studies, we used primarily the 95% W-3.5% Ni-1.5% Fe composite composition which has approximately 13 vol. % molten matrix during the sintering process. To facilitate comparison, we made up composites containing either 13 vol. % Cu or 13 vol. % Au. The procedure was changed slightly in that the presintering operation was

omitted. Instead, the mixed powders were pressed into a ceramic mold and heated to 1625 K and held for the desired sintering times. This was done because an equivalent presintering temperature with respect to the matrix melting point would be so low as to preclude any significant diffusion in the W. The compacts were sintered for 30 minutes and then examined. These same compacts were sintered an additional 210 minutes, and again examined. The first experiments were done with W-Cu but the results were considered subject to some uncertainty because of the large density difference between the Cu and W which could cause some separation or settling of the W to the bottom of the compact, and because of the high vapor pressure of Cu (~ 0.1 mm at 1625 K) which could result in serious compositional changes during long-term sintering. Gold is much less objectionable on both of these points, so it was used for the second series of experiments. The change in spheroid size as a function of sintering time is shown in Fig. 18 along with our earlier results on the 95% W-3.5% Ni-1.5% Fe composite sintered at 1875 K, and Krock's¹⁸ on an 85% W-10.5% Ni-4.5% Fe composite sintered at 1735 K. Note that the slopes of the spheroid growth vs time plots are similar to those for W sintered with Ni + Cu. If one calculates the activation energy for growth using the assumption that the mechanisms

are the same and comparing the times required for the 95% W and the 85% W composites to reach $10\text{ }\mu\text{m}$, and the 85% W and W-Au to reach $2\text{ }\mu\text{m}$, then one gets 256 kcal and 199 kcal, respectively. This similarity in activation energies could indicate that the growth mechanisms are the same. Typical microstructures of the W-Cu and W-Au composites after 4 hours sintering are shown in Figs. 19a through 19d. Their spheroid size distributions are shown in Fig. 20. An unexpected occurrence increased the informational output in the W-Au run. During the early stages of sintering, the shrinkage was quite high because of the omission of a pre-sintering treatment, and the central portion of the top part of the compact caved in. This motion forced contact between many of the W spheroids. In this zone, which had about 500 spheroids showing on the polished surface, the spheroids were quite large, about $17\text{-}\mu\text{m}$ diameter as opposed to $2\text{ }\mu\text{m}$ for the remainder of the compact, and about 12% of these were larger than $25\text{ }\mu\text{m}$. After 210 minutes additional sintering, the average spheroid diameter on a new plane through this zone was just slightly greater than $18\text{ }\mu\text{m}$. Several spheroid diameters were removed to insure against surface effects which might result from the second sintering, so an entirely different section of this anomalous zone was being examined. Therefore, we cannot make a conclusive statement about the rate of spheroid growth in this zone. Typical structures after 30- and 240-minutes sintering are shown in Figs. 21a through 21d. This shows that rapid spheroid growth is possible since more than 100 "average" size spheroids in this composite were required to make just one of these averaged sized large ones in the anomalous zone. The structural appearance is similar to that for W-Ni-Fe composites, and shows that agglomeration or coalescence and the shape change toward spherical take place rapidly. Obviously, spheroid growth here is not by the dissolution and reprecipitation process.

Fig. 18. Spheroid growth as a function of time for W-Cu and W-Au composites compared with two W-Ni-Fe composites.

Fig. 19. Microstructures of W-Cu and W-Au composites after 4 hours sintering at 1625 K: a) W-Cu, b) W-Cu, c) W-Au, and d) W-Au.

Fig. 20. Spheroid size distributions for W-Cu and W-Au composites sintered at 1625 K.

F. Spheroid Growth by Coalescence

A number of the experiments already described indicate that coalescence of spheroids is one of the mechanisms for spheroid growth. Assuming two spheroids combine, grain boundary migration and the trend toward sphericity will be rapid. Therefore, the process must be stopped at precisely the proper time to show the combination of two or more spheroids taking place. The number of combinations taking place at any particular time can be increased by inducing movement of the spheroids, such as sintering while the compact is being vibrated. We chose a simpler technique whereby we would get an exaggerated amount of spheroid contact at

Fig. 21. Large spheroids formed during sintering W-Au after 30 minutes and after 240 minutes: a) sintered 30 minutes, b) sintered 30 minutes, c) sintered 240 minutes, and d) sintered 240 minutes.

any time during the sintering process. A composite containing 89% W-7.7% Ni-3.3% Fe was chosen for this experiment because with this Ni:Fe ratio, the chemical composition of the matrix and of the spheroids would be the same as for our other composites. The only difference would be a larger matrix volume. The zone furnace was used in a stationary mode so that only ~ 2 mm of the central section of the piece would be at the maximum temperature, and this was held at 1875 K. Because of the increased volume of molten matrix, the composite could not support itself, and the specimen slumped during the sintering operation. This movement was sufficient to force a large number of spheroids to come into contact, and those coming into contact with the proper

crystallographic orientation welded together. The specimen was then cooled rapidly so that many spheroid combinations would not have sufficient time while surrounded by molten matrix to become spheroidal. The microstructures of this slumped zone showed two important features. First, many of the spheroids did combine, and secondly, the average spheroid size in the slumped zone was larger than that of the 95% W composite sintered under similar conditions even though the increased matrix volume should result in decreased spheroid growth. A number of examples of spheroids which have combined as well as some that are growing preferentially in the direction of the slumping movement are shown in Figs. 22a through

22d. This shows that coalescence is not only a viable mechanism for spheroid growth, but probably a very important one. There are a number of factors which could influence spheroid growth if coalescence were the predominant method. Larger spheroids have greater surface areas, possibly increasing their chance for contact with other spheroids. Furthermore, if the angle of contact is critical for coalescence,⁵ then larger spheroids would have more 'active' surface area. Smaller spheroids have more freedom of movement and rotation while surrounded by the matrix. In this study, we assumed that the combination of two spheroids by coalescence was the result of a random collision. The

spheroid size distribution for a specimen sintered at 1873 K for 1.3 minutes, and for this same composition for longer sintering times is shown in Fig. 23. We used the spheroid size distribution of this composite sintered for 1.3 minutes as our starting composite for our computer study of spheroid growth based strictly on random contact for coalescence. Each particle was assigned a number, and the order of coalescence was determined by a random number generator. The volumes of the two coalescing particles were added and the diameter of the 'new' particle determined. The 'new' particle was assigned a number, and the entire process repeated. After each group of 50 such combinations,

Fig. 22. a-d) Examples of coalescence of spheroids during liquid-phase sintering.

Fig. 23. Spheroid size distribution as a function of sintering time for the 95% W-3.5% Ni-1.5% Fe composite sintered for various times at 1873 K.

the average spheroid size and the size distribution for this hypothetical composite were determined. The spheroid size distributions for a number of average spheroid sizes are shown in Fig. 24. Note that the trend of the spheroid size distributions for such a random choice coalescence in the hypothetical composite is very similar to that obtained for experimental tests using longer sintering times. In particular, note the similarity of the distributions where random coalescence gave an average spheroid size of $24.31 \mu\text{m}$ with the experimental run at a sintering time of 32.5 minutes which had an average spheroid size of $23.67 \mu\text{m}$. The computer program was terminated once the trend was established because too few particles remained for a reasonable distribution. For example, about 240 of the original spheroids are required to form just one $30\text{-}\mu\text{m}$ -diameter spheroid. This problem could be

Fig. 24. Computer-generated spheroid size distributions after random combinations of two spheroids repeatedly for the composite originally sintered 1.3 minutes in Figure 23.

circumvented easily by multiplying the original number of spheroids by 100 or so, but this increases the computer time required significantly.

Other computer programs were tried where particles were weighted on the basis of surface area or radius to favor the coalescence of larger spheroids, and on the basis of mobility to favor coalescence of the smaller spheroids, but the results were not compatible with experimental results.

IV. DISCUSSION

The spheroid growth mechanism for liquid-phase sintered composites has been studied by a large number of investigators over the past forty years. Most studies have been on time and temperature effects, and on the fundamental growth

mechanisms. Spheroid growth based on the dissolution of small spheroids with simultaneous precipitation of the high-melting component from the liquid matrix onto the larger spheroids with the differences in surface energy between the large and small spheroids providing the driving force, as first proposed by Price *et al.*,¹ is still the most generally accepted theory. However, a few different theories, such as coalescence of particles in the molten matrix, coalescence during certain stages of sintering, etc., have been proposed. However, these theories are based on spheroid growth rates at different sintering temperatures. Unfortunately, a lot of the experiments began with specimens which were in the presintered condition, and the assumption was made that after short periods of liquid-phase sintering at different temperatures, all structures were equivalent.

This program was designed to obtain direct experimental evidence on the spheroid growth mechanism because future progress on liquid-phase sintered alloy development is strongly dependent on a basic understanding of the growth process.

The importance of starting all tests with the same, well-characterized basic material was amply demonstrated when it was shown that the spheroid growth rate was not that predicted theoretically, the temperature effect very inconsistent, and there was no trend toward growth rate adjustments for runs using liquid-phase sintered specimens which were sintered additionally at different temperatures. All this was circumstantial evidence against dissolution and precipitation being the predominant growth mechanism. Sintering with a floating zone gave oriented growth for only about two particle diameters, again indicating that precipitation of W from the melt was not necessarily at the point of lowest energy.

Resintering of sintered composites which had been cold-worked results in recrystallization and subsequent grain boundary attack of the surface grain boundaries to such an extent that many of the recrystallized grains were separated from the parent

grain. Thus, total spheroid energy content can overwhelm the effects of surface energy.

Tungsten particles do form in matrix pockets, and such particles tend to coalesce, as evidenced by the nonspheroidal shape of many such particles. Furthermore, particles tended to form in matrix pockets adjacent to larger spheroids in preference to areas away from them. If the dissolution and precipitation mechanism were predominant, then we would simply expect more rapid growth of the larger spheroids and little if any formation of new small spheroids.

Cleavage of large spheroids shows that many of them contain matrix pockets which are completely surrounded by tungsten. Many of these pockets were as large as 10 μm in diameter. It is impossible to form such a geode-like structure during growth by precipitation.

Experiments using either copper or gold as the molten matrix during liquid-phase sintering show that spheroid growth takes place at rates similar to the other systems when sintering temperature is considered even though tungsten and copper are mutually insoluble as is tungsten and gold. Furthermore, rapid spheroid growth is possible if spheroid contact is encouraged, and large spheroids are formed. The results from these experiments leave no doubt that spheroid growth can and does take place in instances where it is impossible for the dissolution and reprecipitation mechanism of spheroid growth to be operative.

An experiment designed to increase spheroid contact shows that coalescence does occur, and since spheroid growth by such a mechanism would be rapid, coalescence is probably the predominant growth mechanism even though other growth mechanisms are probably operating simultaneously.

V. CONCLUSIONS

Spheroid growth during liquid-phase sintering is predominantly by the proper contact and coalescence of two or more spheroids, even though

other growth mechanisms may be operating simultaneously.

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