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LIQUID PHASE SINTERING OF W-Ni-Fe IN A TEMPERATURE GRADIENT

by

Eugene G. Zukas and Leonard S. Levinson

ABSTRACT

During the liquid-phase sintering of W-Ni-Fe composites, solid tungsten single crystal spheroids are surrounded by a molten matrix of W-Ni-Fe. These spheroids grow in a regulated manner if either the sintering time is increased or if the sintering temperature is raised. Since the slope of the log diameter-log time plot is $1/3$, and should remain constant because it is based on the dissolution of tungsten from the small spheroids with simultaneous precipitation of tungsten from the molten matrix onto the larger spheroids, one should be able to characterize the behavior of any new composite composition by just one sintering experiment in a calibrated temperature gradient.

A low matrix volume composite (95% W-3.5% Ni-1.5% Fe) sintered in a temperature gradient showed anomalous behavior in that the spheroid size did not decrease with decreasing temperature in the gradient, and the average spheroid size was much larger than expected based on constant sintering temperature experiments. Furthermore, composites of higher matrix volume (92% W or 89% W with the same nickel to iron ratio) behaved differently in that they had a smaller average spheroid size at the lower temperatures in the gradient. Since copper and tungsten are mutually insoluble, and since copper is dissolved readily by the matrix, copper was injected into both presintered and liquid-phase sintered composites to follow matrix flow during subsequent sintering treatments. The copper concentration decreased with distance from the hot zone for high volume matrix alloys, pretty much in accordance with liquid diffusion theory, but in the low volume matrix alloys where the volume of solid tungsten spheroids is higher and should impede matrix motion even more, the copper was distributed almost uniformly throughout the matrix that was molten during the sintering. Since the spheroid compositions, matrix compositions, matrix densities, spheroid surface tensions, matrix surface tensions, and most other properties are the same for all specimens, the seemingly anomalous behavior is attributed to some mechanism dependent on capillary action since the decreased pore radius between the spheroids in the low matrix volume composites increases the capillary forces by about 25%.

INTRODUCTION

When tungsten-nickel-iron composites containing from 80 to 95% W are liquid-phase sintered, the resulting structure consists of spheroids of essentially pure tungsten embedded in a matrix of W-Ni-Fe. Numerous studies have shown that the average size of the tungsten-rich spheroids in composites of this type increases if a) the sintering time is increased,¹⁻⁵ or b) if the sintering temperature is increased.^{1,2,5} Furthermore, log-log

plots of average spheroid diameter versus time at a constant sintering temperature are straight line plots, and if a series of sintering experiments are done at different temperatures, a series of parallel lines are obtained. The experimental behavior showing the effect of both time and temperature on spheroid growth for a similar W-Ni-Cu composite is shown in Figure 1. The results from these experiments show that the change in spheroid size

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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. 1.

is a continuous function of either sintering time or sintering temperature. The slope of the log time-log size plot is $1/3$, and tends to remain at about this value, supposedly because it is a function of the spheroid growth mechanism for composites of this type.⁶⁻¹⁴ The presently accepted theory is that spheroid growth is controlled by dissolution of the small spheroids with simultaneous precipitation of tungsten from the molten matrix onto the larger spheroids, the process being controlled by the difference in surface energy between the smaller and larger spheroids.

Since the spheroid size during liquid-phase sintering is an orderly function of time, then the behavior of new composites having slightly different compositions should be predictable from the results of a single experiment, or not more than two experimental runs even if the log size-log time plot has a slope different from $1/3$ because of the spheroid growth not being strictly a function of the generally accepted theory. This would be accomplished simply by sintering composites in a calibrated temperature gradient for two different times. The slope of the log diameter-log time plots could be determined from the change in spheroid size with time and the activation energy from the change in spheroid size in the temperature gradient as a function of the temperature in the gradient.

We ran a series of sintering experiments on a well-characterized 95% W-3.5% Ni-1.5% Fe composite to check our theories. The results from our tests

reported herein showed that the high tungsten composites (low matrix volume) have much larger spheroid sizes at the lower temperatures in the gradient than would be predicted from our uniform temperature sintering tests, indicating anomalous molten matrix behavior. In an attempt to determine the reason for this, copper was introduced into the matrix of both presintered and sintered specimens as a tracer element to study matrix motion during the sintering operation. Such experiments are possible since the copper is insoluble in the tungsten particles (15) but is easily dissolved by the matrix. The movement of copper showed anomalous behavior in the high tungsten composite indicating that perhaps some process dependent on capillary action promoted matrix circulation.

II. EXPERIMENTAL TECHNIQUES

The presintered composites were prepared for us by H. Sheinberg of CMB-6. Nickel and iron powder (2.5 and 4.4 μm diameter, respectively) were preblended by rolling in bottles containing agitator wires for 8 hours at 60 rpm. This blend was then added to W-powder, and roll-blended for an additional 8 hours. Being careful to prevent gravity separation, the powders were packed carefully into polyvinylchloride container sacks which were then sealed and evacuated through a hypodermic needle stuck through the lid. The specimens were then isostatically pressed in perforated metal holders at 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 either 1653 K or 1673 K.

The cross-section of the temperature gradient sintering furnace used for these experiments is shown schematically in Figure 2. The graphite tube heater was resistance heated by a high current-low voltage power supply (for example, 3000 A at 9V to achieve 1873 K). The high temperature of the hot zone was about 3 mm wide. The maximum specimen temperature was read by focussing an optical pyrometer directly on the specimen surface through a hole in the reduced section of the heater tube. Sintering was done under a slight positive pressure of helium gas. There was no detectable carbon pickup by the specimens from the graphite heater, except on a few occasions where specimens

Fig. 2 Cross-section of Temperature Gradient Furnace

Fig. 2 Cross-sectional sketch of the temperature gradient furnace with specimen in place for sintering.

accidentally touched the heater, in which case the specimens were discarded after the preliminary microstructural studies. After sintering, the specimens were cooled in flowing helium where about 5 minutes were required to cool below 873 K.

Matrix motion during the sintering process was followed by injecting copper as a tracer on a line source, and mapping the copper concentration on completion of the run. No interference was expected from the W-rich single crystal spheroids since W and Cu are mutually insoluble, and since the Cu dissolves readily in the matrix. Copper was injected into both presintered composites and into

composites which had already been liquid-phase sintered. The test specimens were 0.80 cm diameter by 5.75 cm long. The copper was injected by sectioning the specimen with a silicon carbide cut-off wheel about 1.90 cm from one end and inserting a copper disc 0.80 cm diameter by 0.075 cm thick between the sections. For the sintering part of the experiment, the joint was centered in the hot zone with the specimen in a vertical position, the longer section being above the hot zone. Under these conditions, the top of the specimens never reached the matrix melting temperature.

After sintering, the specimens were mounted in metal clamps so that a plane near the specimen center could be examined metallographically. Almost half of the specimen was removed on a belt sander. The specimens were then ground wet through 600 grit silicon carbide paper, dry polished through 4/0 metallographic paper, polished through 1 μ m diamond abrasive, and electropolished and electro-etched. Each specimen was then placed on the metallograph so that the center of the specimen from the hot zone to the colder areas where the matrix did not melt could be examined on the same traverse. Contiguous photographs were taken of a 350 μ m wide strip in 450 μ m segments. Each photograph at 254X was placed under a one-matte sided transparent tracing paper and the diameter of each spheroid measured with a ruler where each marked division represented 2 μ m on the photograph. The spheroid diameters were estimated to the nearest 1 μ m. Non-symmetrical cross sections were represented by numbers which would be diameters for circles having an equivalent cross-sectional area. These are sometimes difficult to evaluate accurately and increase the scatter in the measurements. Each spheroid was marked after measurement so that all spheroids would be measured, but so that none of the spheroids would be measured more than once. There are numerous analyses on particle size measurement¹⁶⁻¹⁹ designed to reduce the time and effort required for analysis, but generally, these introduce a correction factor since such measurements are seldom on the major diameter of the particle cross section visible on the polished surface. Line intercept methods of measurement were tried but these gave excessive scatter, probably because the spheroid size distribution is

not Gaussian. It must be remembered that even in our measurements, we only measured the major diameter of the circular cross section exposed on the polished plane, which again is seldom the actual major diameter of the sphere. This problem was treated mathematically (20) many years ago where for perfect spheres, the average diameter of a spheroid measured on a cross section was calculated to be about 79% of the true diameter. Normally, a correction for this is not made since it generally introduces a constant multiplier in the usual treatment of most data.

For liquid-phase sintered composites, especially those having a low matrix volume, the spheroids are not perfectly formed, as can be seen from the typical scanning electron micrographs shown in Figure 3. Figures 3a and 3b are different areas of fractured surfaces from two different specimens. Figure 4 shows metallographic sections of a gradient sintered specimen where the spheroid size does differ according to the temperature at its location in the temperature gradient. Figure 4a is farther from the hot zone than Figure 4b, and the difference in spheroid sizes is readily apparent. These photomicrographs again emphasize the problem of choosing a diameter which truly represents the diameter of a circle having an equivalent cross section.

The matrix behavior was studied by examining the copper distribution in the matrix. Since the copper content is low on a total volume basis, the analysis must be made by some technique which doesn't allow the presence of the tungsten to mask the copper. Since the copper is present only in the matrix, then elemental analysis by scanning electron microscopy is feasible. It was assumed that iron was uniformly distributed within the matrix and so the copper to iron ratio was used to obtain the copper distribution.

III. EXPERIMENTAL RESULTS

Three 95% W-3.5% Ni-1.5% Fe composites were sintered in a temperature gradient with the maximum temperature of the hot zone at either 1773 K, 1873 K or 1973 K. These specimens were sectioned and the spheroid size determined as a function of distance (and therefore temperature) from the hot zone. The results from the three runs were similar in that the spheroid diameter did not decrease in any systematic way with the temperature decrease in the gradient. Because of the narrow liquid-phase sintered zone for the specimen sintered with a high temperature in the hot zone of 1773 K, and some surface cracking on the one sintered at 1973 K, these specimens were only examined qualitatively. However, the specimen sintered at 1873 K was

(a)

(b)

Fig. 3 Scanning electron micrographs of tungsten spheroids. 3a is from a different specimen than 3b. Intended to illustrate size and shape differences.

(a)

(b)

Fig. 4 Photomicrographs of a metallurgical section of a specimen of high volume matrix sintered in a temperature gradient. a) 16.65 m^{-3} from the hot zone and b) 9.00 m^{-3} from the hot zone.

Fig. 5 Spheroid diameters of 95% W-3.5% Ni-1.5% Fe composites as a function of distance from the hot zone after normal sintering, and after sintering with copper added to trace matrix movement. Sintered with the maximum temperature in the zone at 1873 K.

studied in great detail, and the spheroids photographed over the entire length of the traverse were measured and treated statistically. A plot of spheroid diameter versus distance from the hot zone for this specimen is shown in Figure 5. A similar specimen in the presintered condition was cut and a copper disc inserted to trace the matrix flow in the hope that this might give some clue to the spheroid size anomaly in temperature gradient sintering. The sintering time was reduced to one hour to limit copper diffusion and maximize the concentration gradient of the copper even though this would mean that the average particle size would be much smaller. Surprisingly, the sintering behavior was completely different in that the spheroid size decreased as the temperature in the temperature gradient decreased. This change in spheroid diameter with distance from the hot zone is also shown in Figure 5. Since spheroid growth is dependent on the volume change, and is considerable for small diameter changes at the larger sizes, perhaps this parameter would be more sensitive to the variables, especially at the larger spheroid diameters. According to Kothari,¹ the volume change would give similar results to those from a diameter change, Figure 6, and in fact, he used diameter to the third power for his activation energy calculations. The volumes of the average size spheroid for our two experiments as a function of distance from the hot zone are shown in Figure 7.

Fig. 6 The change in volume with sintering time or temperature from Kothari's work (1) on the 89% W-7% Ni-4% Cu composite.

Fig. 7 Spheroid volumes of 95% W-3.5% Ni-1.5% Fe composites as a function of distance from the hot zone (or temperature) after normal sintering, and after sintering with copper added to trace matrix movement. Sintered with the maximum temperature of the zone at 1873 K.

Regardless of whether spheroid diameter or volume is considered, the conclusions are the same, i.e., in normal sintering, the spheroid size does not decrease as much as expected for those portions of the specimen which are in the lower temperature sections of the gradient. However, the anticipated behavior of decreasing spheroid size with decreasing temperature occurred when a copper disc was injected to trace matrix flow. Since copper and tungsten are mutually insoluble, and since the copper is readily soluble in the matrix, then perhaps the anomalous behavior could be attributed to the change in matrix volume resulting from the solution of the copper disc or to the decrease in the solubility of the tungsten in the matrix. The possibility that this effect was caused by increased matrix volume was further investigated by gradient temperature sintering three compositions. These were 1) 95% W-3.5% Ni-1.5% Fe (a repeat on a different batch of material), 2) 92% W-5.6% Ni-2.4% Fe and 3) 89% W-7.7% Ni-3.3% Fe. The maximum temperature in the hot zone was increased to 1973 K to increase the length of specimen which would undergo liquid-phase sintering even though some surface cracking was inevitable. Plots of spheroid diameter versus distance from the hot zone (or temperature) for two of the composites are shown in Figure 8, and their average volumes versus distance in Figure 9. In agreement with the earlier results, the spheroid size of the 95% W composite did not decrease in accordance with the sintering temperature. However, the spheroid size of the 92% W composite did decrease. The spheroid size of the 89% W composite also decreased with distance from the hot zone, but because of the high liquid content during sintering, the specimen slumped almost 15%. This slumping changed the position of the different areas in the hot zone, and added a further complication in that some zones were sintered at different temperatures while the zones at the lower temperatures, i.e., just above the matrix melting temperature, may have been molten for only part of the sintering cycle. All of these factors tend to exaggerate the change in spheroid size with distance from the hot zone, and so the results were considered somewhat inaccurate from a quantitative standpoint. These results suggested

Fig. 8 Spheroid diameters of 95% W-3.5% Ni-1.5% Fe and 92% W-5.6% Ni-2.4% Fe as a function of distance from the hot zone (or temperature) after sintering. Sintered with the maximum temperature of the hot zone at 1973 K.

Fig. 9 Spheroid volumes of 95% W-3.5% Ni-1.5% Fe and 92% W-5.6% Ni-2.4% Fe as a function of distance from the hot zone (or temperature) after sintering. Sintered with the maximum temperature of the hot zone at 1973 K.

that the anomalous behavior was related to matrix volume (just as in the experiments described earlier where copper dissolved in the matrix and increased its volume) unless there was some unexpected change in spheroid size distribution which would not be evident from average diameter measurements. Plots of spheroid size distribution for various distances from the hot zone are shown in Figure 10 for the 95% W composite sintered at 1873 K, and in Figure 11 for the 95% W composite sintered at 1973 K. These plots show that for the 95% W composite, the average spheroid size and the size distributions of the spheroids are about the same over fairly wide temperature differences in the temperature gradient. On the other hand, for the 95% W composite where the matrix volume was increased by the injection of copper before any liquid-phase sintering occurred (Figure 12), and for the 92% W composite where the matrix composition was the same but the matrix volume greater (Figure 13), the average spheroid diameter and the

Fig. 10 Spheroid size distribution as a function of position in the temperature gradient for the 95% W-3.5% Ni-1.5% Fe composite sintered with the maximum temperature in the gradient at 1873 K.

Fig. 11 Spheroid size distribution as a function of position in the temperature gradient for the 95W-3.5 Ni-1.5 Fe composite sintered with the maximum temperature in the hot zone at 1973 K.

spheroid size distribution are different for different zones in the temperature gradient. At the lower temperatures, there are a greater number of small spheroids and a smaller number of large ones. The trend of spheroid growth with increasing temperature in the temperature gradient is readily discernable.

The use of copper as a tracer element to study matrix behavior for specimens in the presintered condition is of limited value if the matrix volume

Fig. 12 Spheroid size distribution as a function of position in the temperature gradient for the 95W-3.5 Ni-1.5 Fe composite after copper had been injected and the matrix volume increased. Sintered with the maximum temperature in the gradient at 1873 K.

Fig. 13 Spheroid size distribution as a function of position in the temperature gradient for the 92W-5.6 Ni-2.4 Fe composite sintered with the maximum temperature in the gradient at 1973 K.

is small because its introduction and dissolution preferentially in the matrix serves to increase the matrix volume and to decrease the tungsten solubility during the formation and early growth of the spheroids. However, these difficulties can be circumvented by injecting copper into composites which have already been fully sintered in the presence of a liquid phase, and where further spheroid growth with increasing sintering time is slow. Copper was injected 1) into a fully sintered 95W-3.5 Ni-1.5 Fe composite which was then re-sintered in a temperature gradient with the hot zone at 1623 K, well above the melting point of copper but below the melting point of the matrix, 2) into a fully sintered 95W-3.5 Ni-1.5 Fe composite which was then re-sintered in a temperature gradient where the hot zone was at 1873 K, well above the matrix melting point, 3) into a fully sintered 92W-5.6 Ni-2.4 Fe composite which was then re-sintered in a temperature gradient where the hot zone was held at 1873 K, and 4) into a presintered 95W-3.5 Ni-1.5 Fe composite which was then sintered in a temperature gradient where the hot zone was held at 1873 K. Since the copper stays completely in the matrix, the analytical techniques must be insensitive to the presence of the tungsten spheroids which comprise over 80% of the composite volume in order to monitor compositional changes along the longitudinal axis of the specimen. Analytical

Fig. 14 Copper concentration as a function of distance from the hot zone for composites which were injected with copper to trace matrix behavior. The composites have different matrix volumes or were sintered at different temperatures.

analysis can be done readily on patches of pure matrix between the spheroids with the scanning electron microscope since the effective beam diameter is less than a micron, but there is a small amount of scattering from brass components and other surfaces in the machine. We used the ratios of the copper and iron peaks. The plots of copper concentration versus distance from the hot zone for the various specimens are shown in Figure 14. For the specimen re-sintered above the melting point of copper but with the matrix solid, the copper diffusion was very slow. For the 95% W re-sintered with the hot zone at 1873 K, the copper concentration was almost uniform for a considerable distance, essentially independent of the temperature gradient. The other specimens showed a decrease in copper concentration with distance from the hot zone, typical of normal diffusion behavior.

IV. DISCUSSION

When composites of the W-Ni-Fe or W-Ni-Cu types are liquid-phase sintered, the growth of the solid spheroids is dependent on both temperature and time. Since the growth rate is linear on a log-log plot for a single sintering temperature, and since different sintering temperatures give data that plot as parallel lines for different times, then it should be possible to map out the entire sintering behavior of a new alloy composition with a single sintering run in a calibrated temperature

gradient, assuming that the slope of the log size-log time plot is mechanism dependent and has a slope of 1/3. If one is not willing to accept the slope of the log size-log time plot as 1/3 for new composite compositions, then two runs should be adequate. To examine this thesis, a sintering run in a temperature gradient was done using a 95% W composite. The spheroid size did not decrease in the expected manner with the lowering of the sintering temperature in the gradient. However, for a composite containing only 92% W, the spheroid size did decrease with decreasing temperature. Since such composites contain pure W-single crystals embedded in a W-Ni-Fe matrix, then lowering the W-content while keeping the nickel to iron ratio constant should not change the chemical composition of either the W spheroids or the matrix, but should just increase the matrix volume. Therefore, this seemingly anomalous behavior must be strictly dependent on matrix volume. Injecting copper, which remains entirely in the matrix, should serve as a tracer and give information on the matrix behavior during sintering. In presintered specimens of 95% W, the copper alloyed with the nickel and iron during the early stages of sintering, thereby increasing the matrix volume and perhaps changing its chemical composition during the formation of the spheroids and during the early stages of the spheroid growth process. The analytical results showed a concentration gradient of the copper with the copper

content decreasing with decreasing temperature (or increasing distance) from the injection source, pretty much as would be expected from the usual diffusion theories. A similar behavior was noted when the copper was injected into an already-sintered specimen having a larger matrix volume. However, in the low matrix volume composite (95% W) which had been liquid-phase sintered prior to the copper injection, the copper was almost uniformly distributed through most of the temperature gradient.

The results from the experiments already described showed that the matrix in the low matrix volume composites circulates much more during the liquid-phase sintering process than it does in the other composites having a higher matrix volume even though the mechanical resistance to flow should be

greater because of the higher volume of solid tungsten spheroids. There are not many mechanisms known at the present time which are consistent with the observed behavior. In all cases, the temperature gradient, chemical composition of the matrix and the spheroids, density, surface tension of the tungsten spheroids and the surface tension of the matrix should be essentially equal. A possible explanation could be matrix movement caused by capillary action as a result of surface tension forces. The 95% W alloy has about 12% by volume of matrix while the 92% W composite has about 19%. If we assume that we have the same number of pores for specimens having equivalent spheroid sizes, then the capillary forces for the 95% W would be about 25% greater than those in the 92% W simply on the basis of the reduction in the average pore radius. The matrix movement caused by the capillary forces could be enhanced by surface-to-center temperature gradients, and matrix circulation could be quite extensive.

Matrix circulation in the low volume matrix composites could explain their consistently high sintered densities. Similarly, the inability to achieve high densities for tungsten liquid-phase sintered with only copper as the matrix might be attributable to the lack of liquid matrix circulation because of the low surface tension forces.

V. SUMMARY

The liquid-phase sintering behavior of W-Ni-Fe composites having low matrix volume is anomalous in that at least where temperature gradients exist, there is rapid matrix circulation. This behavior tends to produce a uniform average spheroid size distribution and is probably responsible for the high densities achieved during the liquid-phase sintering of such composites. Increasing the matrix volume slightly reduces the matrix circulation and lower average spheroid sizes are found in areas which are at the lower temperatures when sintering is done in a temperature gradient.

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