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Matrix motion of low-volume matrix W–Ni–Fe composites sintered in a temperature gradient

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A low matrix volume (13%) composite liquid-phase sintered in a temperature gradient showed anomalous behaviour in that the spheroid size did not decrease as predicted with decreasing temperature, and the average spheroid size was larger than expected based on uniform temperature sintering experiments. Furthermore, similar composites with higher matrix volume (20 or 28%) had smaller average spheroid sizes at lower temperatures in the gradient. Copper was injected as a tracer into both presintered and liquid-phase sintered composites to study matrix flow during subsequent sintering treatments. The copper concentration decreased with distance from the hot zone for high volume matrix composites, but in the low volume matrix composites where the volume of solid tungsten spheroids was higher (greater resistance to matrix motion), the copper was distributed almost uniformly throughout the matrix. The spheroid and matrix compositions, densities, surface tensions, and most other properties were the same, whereas only the matrix volumes were different. This anomalous behaviour was attributed to some mechanism aided by capillary action since the smaller distances between spheroids in the low matrix composites increase the capillary forces by about 25%.

1. Introduction

When tungsten–nickel–iron composites containing from 80 to 95% tungsten are liquid-phase sintered, the resulting structure consists of bcc tungsten spheroids embedded in a fcc matrix of W–Ni–Fe. Numerous studies have shown that the average size of the tungsten 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 lines, and if a series of sintering experiments are done at different temperatures, a series of parallel lines are obtained. This behaviour is nicely demonstrated by the experimental results of Kothari [1]. The slope of a log diameter–log time plot is $\frac{1}{3}$, and tends to remain at about this value in agreement with theoretical predictions based on 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 driving force being supplied by the difference in surface energies between the small and larger spheroids. Since the spheroid growth rate for a single sintering temperature is controlled by the growth mechanism (slope of log D versus log $t = \frac{1}{3}$), one should be able to predict the behaviour of new composites from the results of a single experiment. This would be accomplished simply by sintering the new composite in a calibrated temperature gradient. Thus, the effect of temperature could be determined from the activation energy for spheroid growth which is readily calculable from the change in spheroid size in the temperature gradient as a function of the temperature in the gradient.

A series of sintering experiments was run in calibrated temperature gradients 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 uniform temperature sintering tests, indicating anomalous molten matrix behaviour. Copper was introduced into the matrix of both presintered and sintered specimens as a tracer element to study matrix motion during the sintering operation in an attempt to explain this behaviour. Such experiments are possible since copper is insoluble in the tungsten particles [15] but is readily dissolved in the matrix. The movement of copper showed anomalous behaviour in the high tungsten composite indicating that capillary action promoted matrix circulation.

2. Experimental techniques

Nickel and iron powders (2.5 and 4.4 μm diameter, respectively) were preblended, and then blended with 1 μm W-powder. The powders were isostatically pressed at 345 MPa (50 000 psi) into compacts which were placed on alumina supports and presintered for 2 h in dry hydrogen. The compacts were then either sintered in a temperature gradient, or sintered uniformly at 1873 K followed by resintering in a gradient.

The cross-section of the temperature gradient sintering furnace used for these experiments is shown schematically in Fig. 1. The graphite tube heater was resistively heated by a high current-low voltage power supply. There was no detectable carbon contamination of the specimens from the graphite heater. The maximum specimen temperature was read by focusing an optical pyrometer directly on the specimen surface through a hole in the reduced section of the heater tube. The melting temperature of the matrix was 1735 K, and its junction with non-melted matrix could be determined easily by metallographic techniques. The temperature gradient in the specimens was determined from the positions of these two temperatures on the specimen adjusted to match the measured gradient on a solid specimen. Sintering was done under a slight positive pressure of helium gas. After sintering, the specimens were rapidly cooled by flowing helium.

Matrix motion during the sintering process was traced by injecting copper, and mapping the copper distribution 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. 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 cutoff wheel about 1.90 cm from one end and inserting a 0.075 cm thick copper disc. The joint was centred in the hot zone with the specimen in a vertical position, the longer section being above the hot zone. Under these conditions, the upper portions of the specimens never reached the matrix melting temperature, a requirement for determining the temperature gradient.

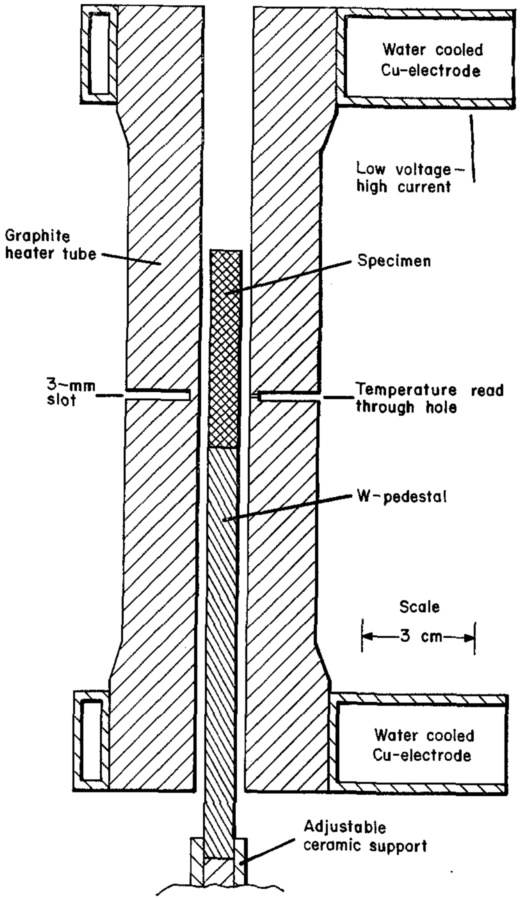

Figure 1 Cross-sectional sketch of the temperature gradient furnace with specimen in place for sintering.

After sintering, the specimens were sectioned longitudinally, polished, and etched. Contiguous photographs were taken of a central strip 350 μm wide in 450 μm segments. For each photograph analysed, the diameter of each spheroid was measured. The non-symmetrical spheroid cross-sections were represented by numbers which would be diameters for circles having an equivalent cross-sectional area. The shapes of some typical spheroids are shown in a scanning electron micrograph (Fig. 2). There are numerous analyses on particle size measurement [16-19]

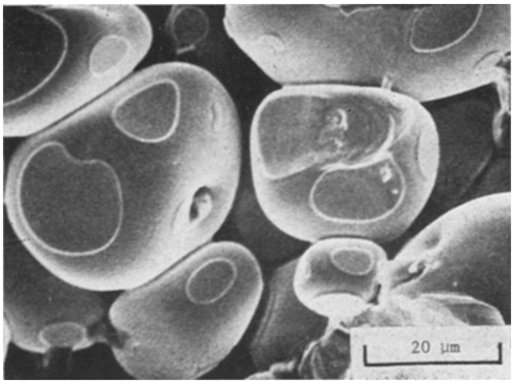

Figure 2 Scanning electron micrograph of tungsten spheroids.

designed to reduce the time and effort of analysis, but generally, these introduce a correction factor. Line intercept methods of measurement were tried but gave excessive scatter.

The movement of the matrix during the liquid-phase sintering process was determined from the final copper distribution. Since the copper is present only in the matrix, elemental analysis by scanning electron microscopy of the matrix pockets is feasible. There are complications in quantitative measurements, but since there is complete miscibility of the matrix components in the liquid state, we assumed that the iron was uniformly distributed throughout the matrix. We used the copper-to-iron ratio to determine the copper distribution.

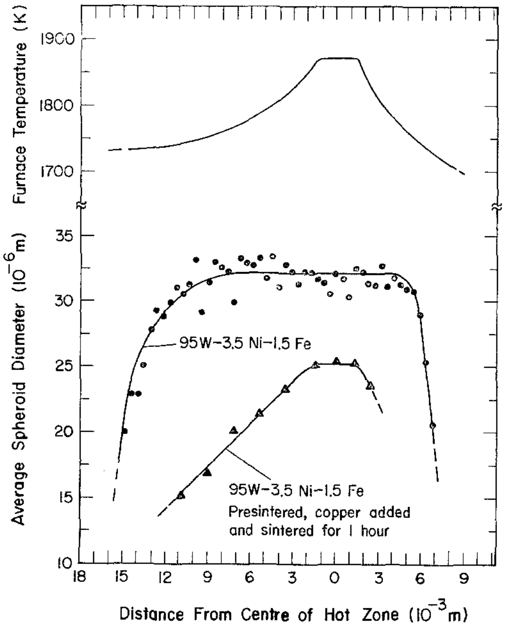

Figure 3 Spheroid diameters of 95% W-3.5% Ni-1.5% Fe composites as a function of distance from the hot zone after normal sintering, and after sintering with copper added to trace matrix movement. Maximum zone temperature at 1873 K.

3. Experimental results

Three 95% 3.5W-% Ni-1.5% Fe specimens were sintered in a temperature gradient with the maximum temperature of the hot zone at either 1773, 1873 or 1973 K. The spheroid size was determined as a function of distance (and therefore temperature) from the hot zone. The results from the three runs were similar in that the average spheroid diameter did not decrease even though the temperature in the gradient decreased. Because of the narrow liquid-phase sintered zone for the specimen sintered at 1773 K, and some surface cracking on the one sintered at 1973 K, these specimens were not studied extensively. However, since many of our earlier sintering experiments were done at 1873 K, the specimen sintered with the hot zone at 1873 K was studied in great detail. The spheroids in contiguous photographs for the entire length of the specimen were measured and treated statistically. A plot of spheroid diameter versus distance from the hot zone for this specimen is shown in Fig. 3. Note that the average spheroid diameter is about the same over the entire temperature range in the gradient where the matrix remained molten. Based on Kothari's analysis [1], the spheroid diameter should have been slightly less than 21 µm at 10 mm from the hot zone, whereas it was actually larger than 32 µm. To see if this anomalous behaviour could be attributed to unusual matrix flow, copper was injected at the hot zone into an identical composite which was sintered under indentical conditions, except that the sintering time was reduced to 1 h to minimize copper evaporation and maximize the copper concentration gradient. The average spheroid size versus distance from the hot zone (or temperature) is also shown in Fig. 3. Note that the average spheroid diameter, unlike that for the preceding run, decreased with distance. Again, based on Kothari's analysis [1], the diameter at 10 mm from the hot zone should be about 16 µm, in excellent agreement with the experimental result. The divergence in results from these two experiments indicated a drastic difference in material behaviour.

There are two obvious possibilities which could explain the difference in behaviour between identical specimens except for the copper injection in one. The copper would alloy with the matrix at the very beginning of liquid-phase sintering and would change the matrix volume as well as its composition. If the results were matrix composition dependent, then tungsten solubility and similar factors would be important. If volume dependent, then matrix flow would be important. The effect of increased matrix volume can be readily assessed by increasing the nickel and iron content of the composite but the ratio of nickel-to-iron must be kept constant, otherwise compositional changes would occur. Three compositions were evaluated. These were (1) 95% W–3.5% Ni–1.5% Fe (a repeat with new materials – 13% matrix volume), (2) 92% W–5.6% Ni–2.4% Fe (20% matrix volume), and (3) 89% W–7.7% Ni–3.3% Fe (28% matrix volume). These specimens were zone sintered with a maximum zone temperature of 1973 K. Plots of average spheroid diameter as a function of distance from the hot zone (or temperature) for the 95% W and 92% W composites are shown in Fig. 4. Again, the average diameter of the low volume matrix composite does not decrease as much as expected with decreasing temperature in the gradient. For example, the average spheroid diameter at 15 mm from the centre of the hot zone for the 95% W composite should be about 20 μm, whereas it was almost 35 μm. The predicted diameter for the 92% W composite should be about 21 μm, whereas it was almost 26 μm, slightly higher than the predicted value. The 89% W composite behaved in much the same manner as the 92% W one, but because of the high liquid matrix content during sintering, slumped almost 15%. This exaggerated the decrease in average spheroid diameter with distance from the hot zone, and so the results were considered somewhat inaccurate from a quantitative standpoint. Clearly then, the anomalous spheroid growth rate is caused by low matrix volume.

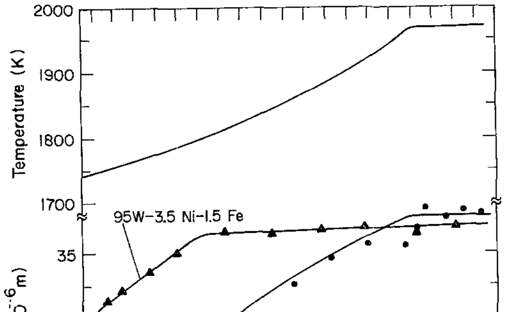

Figure 4 Spheroid diameters of 95% W–3.5% Ni–1.5% Fe and 92% W–5.6% Ni–2.4% Ni as a function of distance from the hot zone (or temperature) after sintering. Maximum zone temperature at 1973 K.

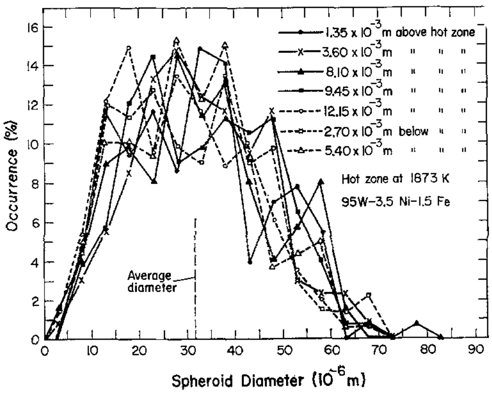

Figure 5 Spheroid size distribution as a function of position in the temperature gradient for the 95% W–3.5% Ni–1.5% Fe composite sintered with the maximum zone temperature at 1873 K.

Plots of spheroid size distribution for various distances from the hot zone are shown in Fig. 5 for the 95% composite sintered at 1873 K. These plots show that not only the average spheroid size, but also the size distributions of the spheroids are about the same over fairly wide temperature differences in the temperature gradient. This was also true for the 95% W sintered at 1973 K. 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 (Fig. 6), and for the 92% W composite where the matrix composition was the same but the matrix volume greater (Fig. 7), the average spheroid diameter and the spheroid size distribu-

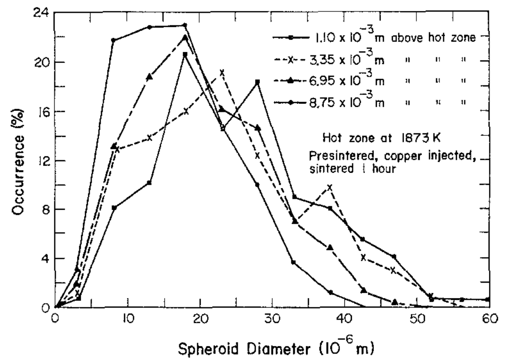

Figure 6 Spheroid size distribution as a function of position in the temperature gradient for the 95%W–3.5% Ni–1.5% Fe composite after copper had been injected and the matrix volume increased. Maximum zone temperature at 1873 K.

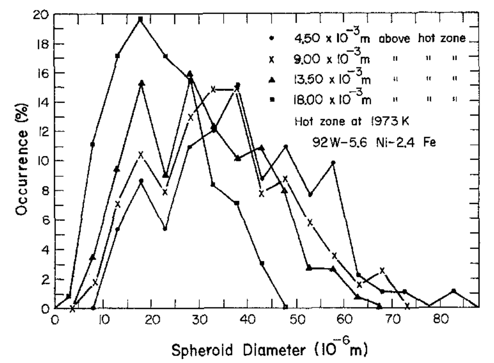

Figure 7 Spheroid size distribution as a function of position in the temperature gradient for the 92% W–5.6% Ni–2.4% Fe composite. Maximum zone temperature at 1973 K.

tion were different for different zones in the temperature gradient. The trend of spheroid growth with increasing temperature in the temperature gradient is readily discernible.

For presintered specimens, the use of copper as a tracer element to study matrix behaviour during sintering is of limited value if the matrix volume is small, because it increases the matrix volume during the formation and early growth of the spheroids. However, this 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 increased sintering time is slow. Copper was injected (1) into a fully sintered 95% W composite which was then resintered 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 (1735 K), (2) into a fully sintered 95% W composite which was then resintered in a temperature gradient where the hot zone was at 1873 K, well above the melting temperature of the matrix, (3) into a fully sintered 92% W composite which was then resintered in a temperature gradient where the hot zone was held at 1873 K, and (4) into a presintered 95% W composite which was then sintered in a temperature gradient with the hot zone at 1873 K. Since the copper stays entirely in the matrix, analytical techniques must be insensitive to the presence of the tungsten spheroids which comprise most of the composite volume in order to monitor changes in the copper content of the matrix along the longitudinal axis of the specimen. Analytical 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. For determining the copper distribution, we used the ratios of the copper-to-iron peaks. The plots of copper concentration versus distance from the hot zone for the various specimens are shown in Fig. 8. For the specimen resintered at 1623 K, the copper diffusion was very limited. For the 95% W resintered 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 behaviour.

4. 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 and has a slope of $\frac{1}{3}$ on a log-log plot for a single sintering temperature, and since different sintering temperatures gives data that plot as parallel lines for different times, then it should be possible to plot the entire sintering behaviour of a new alloy composition from the results of a single sintering run in a calibrated temperature gradient. To examine this thesis, a sintering run was made with a 95% W composite in a temperature gradient. The average spheroid size did not decrease in the anticipated manner at the lower temperatures in the gradient. However, for 92%

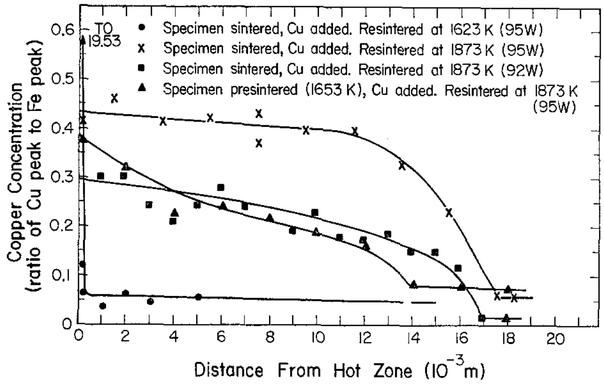

Figure 8 Copper concentration as a function of distance from the hot zone for composites which were injected with copper to trace matrix behaviour. The composites either have different matrix volumes or were sintered at different temperatures.

W, the spheroid size did decrease with decreasing temperature. Since such composites contain W-single crystals embedded in a W–Ni–Fe matrix, then lowering the W content while keeping the nickel-to-iron ratio constant would not change the chemical composition of either the tungsten spheroids or the matrix, but would simply increase the matrix volume. Therefore, this seemingly anomalous behaviour must be dependent on matrix volume. Injecting copper, which remains entirely in the matrix, should serve as a tracer and give information on the matrix behaviour during sintering. In presintered specimens of 95% W, the injected copper alloyed with the nickel and iron during the early stages of sintering, thereby increasing the matrix volume and changing its chemical composition. 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 expected from the usual diffusion theories. Similar behaviour was noted when the copper was injected into an already-sintered specimen having a greater 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 throughout 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 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. For the W–Ni–Fe composites having different matrix volumes, the chemical compositions of the matrices and the spheroids, their densities, surface tensions of the tungsten spheroids and the matrices, and other characteristics should be essentially the same. A possible explanation could be matrix circulation aided by capillary action as a result of surface tension forces. The 95% W alloy has about 13% by volume of matrix while the 92% W composite has about 20%. If we assume that we have the same number of matrix pockets 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 matrix pocket radius. The matrix movement caused by the capillary forces could be enhanced by surface-to-centre temperature gradients, and matrix circulation could be quite extensive.

Matrix circulation in the low volume matrix composites could help 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.

5. Conclusion

The liquid-phase sintering behaviour of W–Ni–Fe composites having low matrix volume is anomalous in that where temperature gradients exist, there is rapid matrix circulation. This behaviour 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 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. The anomalous matrix circulation for low volume matrix composites is probably assisted by capillary forces. Thus, spheroid growth behaviour cannot be predicted reliably from results obtained by sintering in a temperature gradient.

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