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Coarsening of tungsten particles in W-Ni-Fe alloys

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The coarsening kinetics of tungsten particles in W-Ni-Fe alloys during liquid phase sintering was studied. The particle growth rate increased with increasing volume fraction of tungsten, and the growth isotherms followed the cubic rate law, suggesting that the diffusion in liquid phase was the rate-limiting step. However, the particle size distributions were consistent with the reaction-controlled size distribution predicted by the theory of Liftshitz, Slyozov and Wagner. These experimental results could be explained by the diffusion-controlled growth according to the theory developed by Ardell.

1. Introduction

The theory of coarsening kinetics has been extensively developed by Lifshitz and Slyozov [1], and Wagner [2], and is referred to as the LSW theory in this study. The LSW theory is derived based upon the assumption that the volume fraction of solid phase should be sufficiently small, and thus the interaction between particles can be neglected. The particle coarsening rate can be controlled by the diffusion of chemical species between particles (diffusion control), or by the dissolution and precipitation of chemical species on the particle surface (reaction control). In the LSW theory, the growth isotherm of the diffusion-controlled mechanism can be described by the cubic rate law, $r^3 \propto kt$, where r is the mean particle size, t is the time, and k is the growth rate constant, and the square rate law for the reaction-controlled mechanism, $r^2 \propto kt$. In addition, a steady particle size distribution is predicted as sintering progresses for a sufficient period.

It has been suggested by Lay [3] and later developed by Ardell [4] that the effect of volume fraction of solid on particle coarsening should be considered, especially at high volume fraction of solid. As the volume fraction of solid increases, the interaction of diffusion zones between particles becomes more significant, and the diffusion distance becomes shorter; therefore a larger growth rate is predicted for the diffusion-controlled growth. Although the cubic rate law is still valid for the diffusion-controlled growth, the corresponding particle size distribution approaches that of reaction control in LSW as the volume fraction of solid is increased, and becomes exactly the same in the limiting case of unity volume fraction of solid. In general, the predicted particle size distribution of diffusion control closely resembles that of reaction control in LSW for the system containing the volume fraction of a solid not less than 0.2.

Previous studies on W-Ni-Fe alloys by Krock [5], and Kannappan [6] showed that the growth isotherms followed the cubic rate law and concluded that the diffusion of chemical species in the liquid phase was the rate-limiting step during particle coarsening; however, the particle size distributions were not analysed. The purpose of this study is to investigate the coarsening phenomenon of tungsten particles in the W-Ni-Fe system during liquid phase sintering at 1450° C. The coarsening mechanism is determined by comparing the experimental results with the theoretical predictions of LSW and Ardell using the method suggested by Exner and Fischmeister [7]. To understand the effect of the tungsten weight fraction on coarsening kinetics, the specimens containing an equal weight of nickel and iron and various weight fractions of tungsten (90%, 92%, 95%, 97%) are studied.

2. Experimental procedure

The mean particle size of the as-received tungsten powders, measured by sedigraph, was 2.5 μm. The powders were mixed in various weight ratios with 2 wt % paraffin wax in toluene, and then the resulting mixtures were ball-milled for 48 h. After ball-milling, the slurries were dried at 80° C in air for 24 h, and the dried powders were sieved through a 200 mesh screen. The powders were compacted to a cylinder with 3 cm diameter and 0.5 cm height under a pressure of 3×10^4 p.s.i. ($\sim$ 206.7 N mm^{-2}). The green compacts were sintered by using a Lynberg tube furnace with SiC heating elements. To prevent the oxidation of metals, the sintering was conducted under a flowing cracked ammonia atmosphere. The temperature of the furnace was slowly increased at 300° C h^{-1} from room temperature to the pre-sintering temperature of 950° C. The samples were fired at 950° C for 1 h to enhance the combustion of paraffin wax and the reduction of the thin oxide layer on the particle surface before the occurrence of extensive densification. The temperature was then increased at a rate of 200° C^{-1} from 950° C to the sintering temperature

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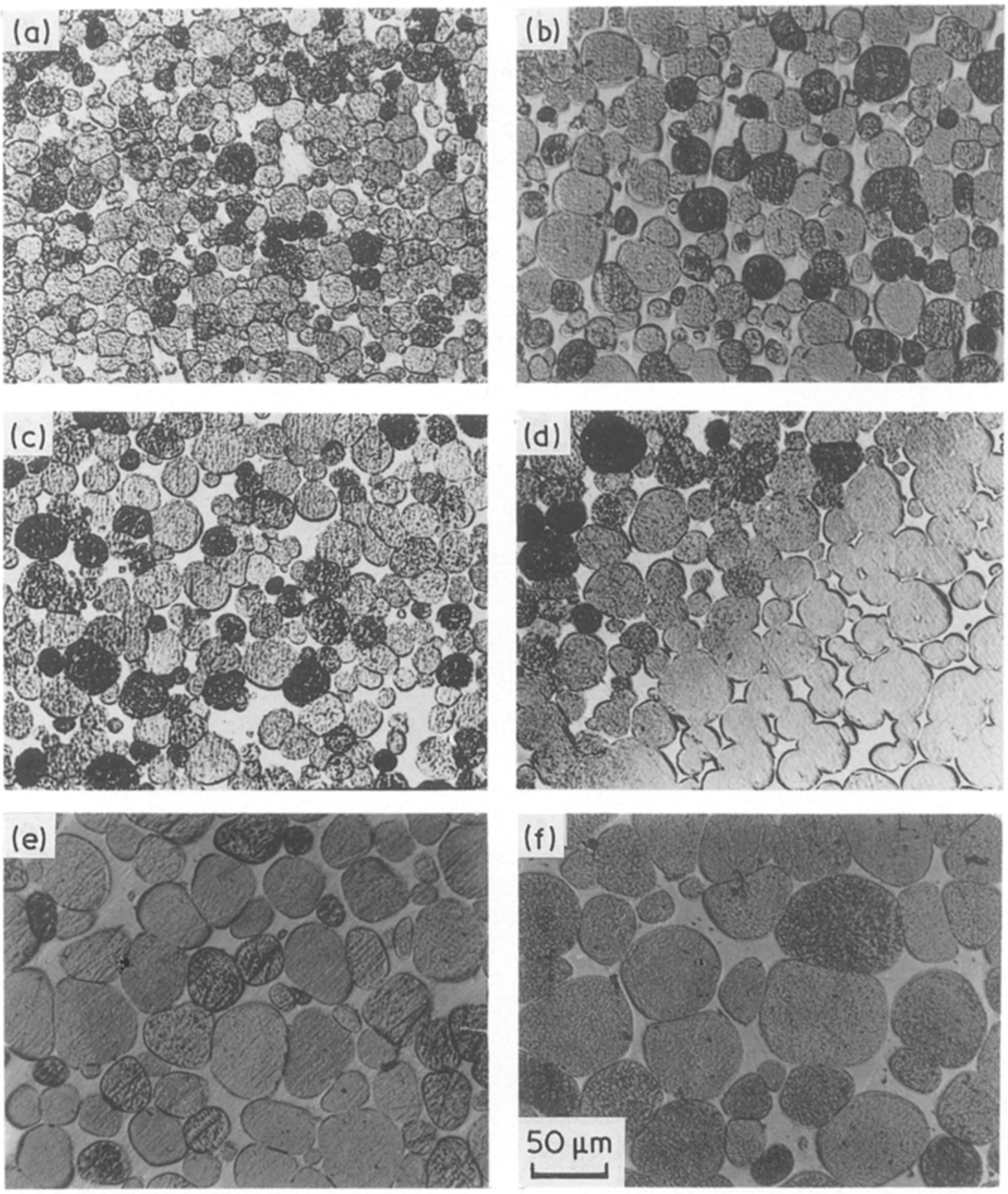

Figure 1 Optical micrographs of 90W–7Ni–3Fe specimens sintered at 1450° C for (a) 10, (b) 30, (c) 60, (d) 120, (e) 300 and (f) 480 min.

of 1450° C. Samples were quenched in air directly from 1450° C after firing for various periods. The densities of sintered compacts were determined in water by Archimedes' method. To reveal the grain boundaries of tungsten, a Murakami solution [8] was used to etch the polished samples. Particle sizes were determined from optical micrographs using a Zeiss point counter, and 1000 particles were measured for each sample to obtain reliable particle size distributions.

3. Results

The specimens are densified very rapidly by liquid phase sintering as soon as the sintering temperature of 1450° C is reached. High sintered densities, > 99% theoretical density, are obtained for the samples sintered at 1450° C for 10 to 480 min. Typical microstructures of the specimens fired for various times are given in Figs 1a to f, and Fig. 1d shows the dark and white areas for the grains etched and unetched by the Murakami solution, respectively. As noted, the rounded tungsten grains are uniformly surrounded by the matrix phase, and no apparent change in the volume fraction of matrix phase is observed with prolonged sintering. By vertical sectioning, it is shown that no tungsten particles sink to the bottom of the specimens during liquid phase sintering.

The typical particle size distributions for the specimens sintered for various times are given in Fig. 2. As can be seen, the particle size distribution moves toward the larger sizes, and becomes broader as the sintering time is increased. The mean sizes are plotted against sintering times at various concentrations of

TABLE I The reciprocal of the slopes for the growth isotherms in Fig. 3

	Composition (wt %)				
	90W–5Ni–5Fe	92W–4Ni–4Fe	95W–2.5Ni–2.5Fe	97W–1.5Ni–1.5Fe	90W–7Ni–3Fe
Slopes	3.18	3.65	3.05	3.05	3.03

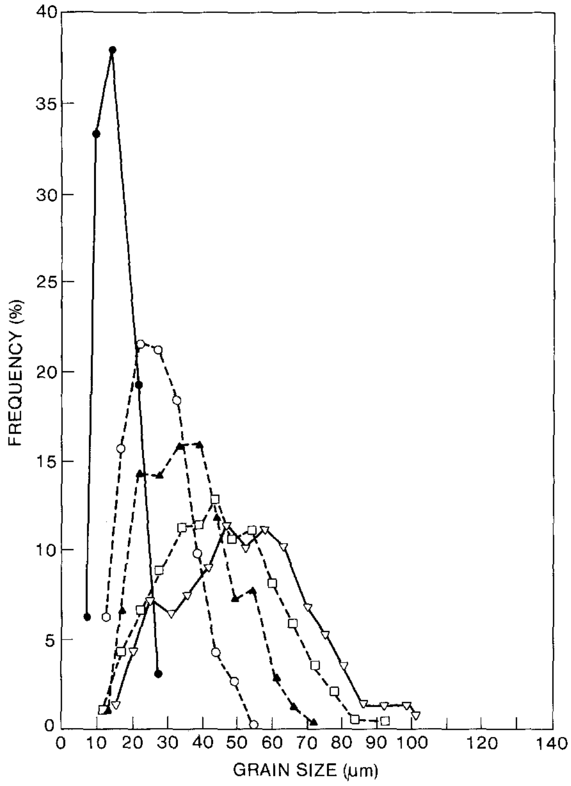

Figure 2 Particle size distributions of 90W–7Ni–3Fe specimens fired at 1450° C for various periods. (●) 10, (○) 60, (▲) 120, (x) 300, (△) 480 min.

matrix phase in Fig. 3, showing that the experimental results can be linearly described by an ln r–ln t relationship. The reciprocal of these slopes in Fig. 3, determined by using a least squares fit method, are very close to 3 for all conditions, as the results show in Table I. This indicates that the growth isotherms can be described by the cubic rate law, and the coarsening is controlled by diffusion. In addition, the mean particle size is larger at a given time as the weight fraction of tungsten is increased for the systems containing 1 : 1 weight fractions of nickel and iron. The mean particle size is also affected by the compositions of matrix phase; a larger particle size is observed for 90W–7Ni–3Fe than for 90W–5Ni–5Fe. By the cubic rate law, the growth rate constant, k, can be calculated and the results are given in Fig. 4. It is evident that the growth rate constant becomes larger for the system

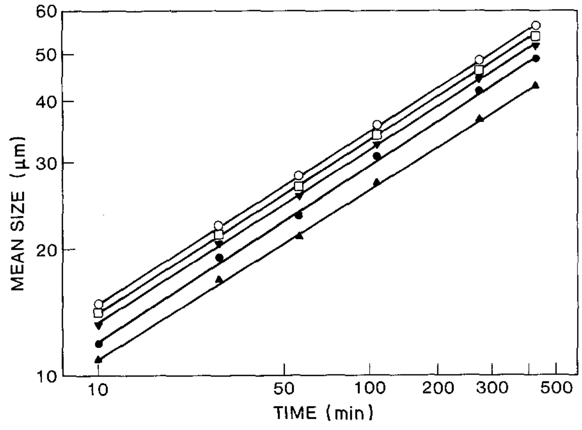

Figure 3 Growth isotherms of (▲) 90W–5Ni–5Fe, (●) 92W–4Ni–4Fe, (▼) 95W–2.5Ni–2.5Fe, (○) 97W–1.5Ni–1.5Fe, and (x) 90W–7Ni–3Fe sintered at 1450° C.

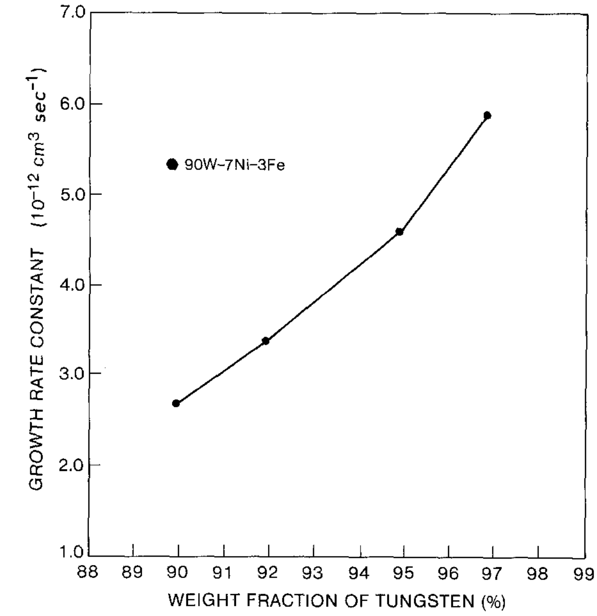

Figure 4 Growth rate constant for the samples with a 1 : 1 weight ratio of nickel and iron various weight fractions of tungsten.

with larger volume fraction of tungsten as the weight ratio of nickel and iron is unity. This is due to the fact that the diffusion distance between particles is reduced with the larger volume fraction of tungsten, and hence increases the growth rate. This provides other evidence that the rate-limiting step during particle growth is the diffusion of chemical species in the liquid phase [4]. It is also found that a larger growth rate constant is obtained for the system of 90W–7Ni–3Fe than for 90W–5Ni–5Fe.

The results shown in Fig. 2 can be replotted as the logarithm of the particle size against the logarithm of cumulative per cent, as shown in Fig. 5. These cumulative size distributions can be linearly described in the range between 10% to 60%. It has been suggested by Moreen [9] that a slope of 4, and 9/4 in the linear section of the cumulative size distribution can be found for the diffusion-controlled and the reaction-controlled growth, respectively. Very good agreement between the slopes of these size distributions and a

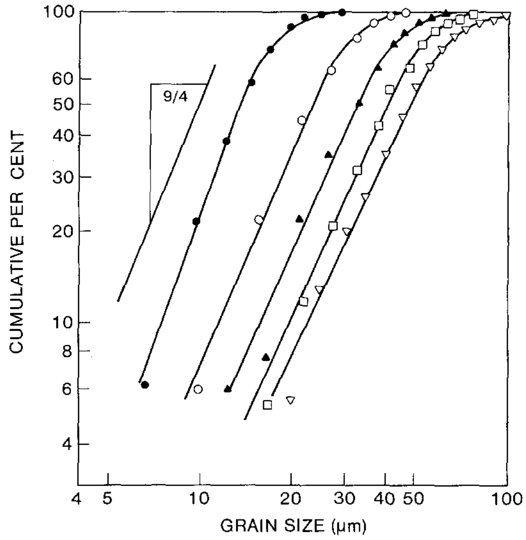

Figure 5 Cumulative particle size distribution of 90W–7Ni–3Fe specimens sintered at 1450° C for various periods. (●) 10, (○) 60, (▲) 120, (x) 300, (△) 480 min.

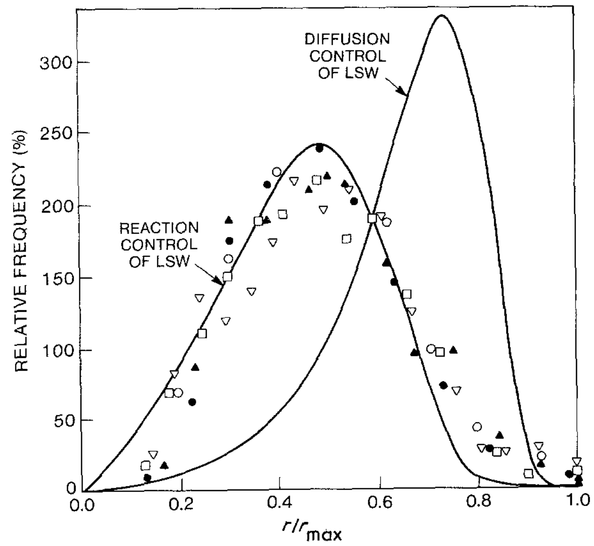

Figure 6 Normalized particle size distributions of 90W–7Ni–3Fe specimens sintered at 1450° C for various periods. (●) 10, (○) 60, (▲) 120, (x) 300, (△) 480 min.

line of slope 9/4 superimposed in Fig. 5 is found, suggesting that the coarsening process is controlled by the dissolution and precipitation of solid on the particle surface. The same results are found for the other conditions in this investigation.

To determine if the particle size distributions have reached the steady state, the observed particle size distributions in Fig. 2 were normalized according to the method suggested by Exner and Fischmeister [7]. Fig. 6 show the typical normalized particle size distributions of the specimens sintered for various times, where the theoretical particle size distributions predicted by LSW are also presented. It is found that the obtained particle size distributions, irrespective of sintering times, significantly follow the reaction-controlled curve of LSW. This phenomenon is shown more clearly in the normalized cumulative particle size distribution, as shown in Fig. 7, indicating that a stationary size distribution is reached even after firing for a short period, 10 min. This observation is consistent with the prediction of LSW theory, and also suggests

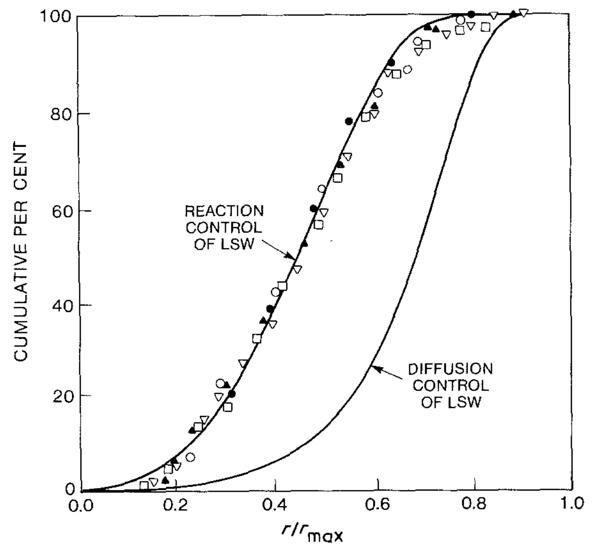

Figure 7 Cumulative normalized size distributions of 90W–7Ni–3Fe specimens fired at 1450° C for various periods. (●) 10, (○) 60, (▲) 120, (x) 300, (△) 480 min.

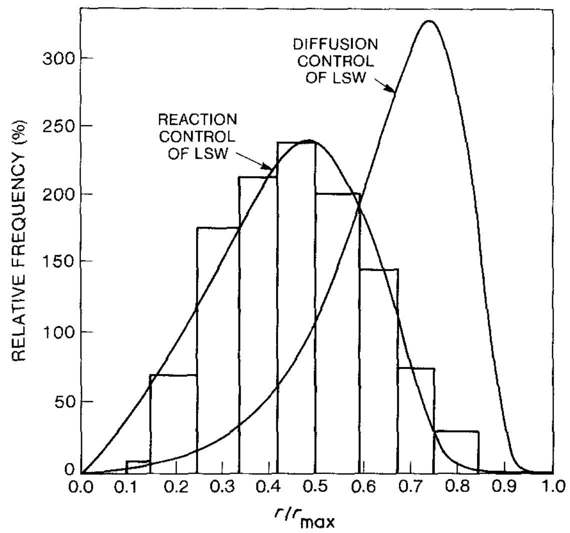

Figure 8 An example of chi-square statistical test for the sample of 90W–7Ni–3Fe fired at 1450° C for 10 min.

that the particle growth is dominated by Ostwald ripening rather than coalescence [1, 2]. To quantitatively determine the goodness of fit between the observed particle size distributions and the theoretical predictions of LSW, a chi-square statistical test was conducted. In this statistical test, a value of $\alpha < 5\%$, or $\alpha > 50\%$ is considered little or significant agreement between observed and theoretical size distributions, respectively. An example is given in Fig. 8, and the calculated α value is 94% for the reaction control and $\ll 0.2\%$ for the diffusion control. The α values for the other conditions are shown in Table II. A very large percentage of α values, $> 65\%$, are greater than 50% for reaction control; however, all of the α values are less than 5% for diffusion control. This indicates that significant statistical agreement is found only between the observed and the reaction-controlled size distributions of LSW.

4. Discussion

It has been reported previously that particle growth could be dominated by coalescence during liquid-phase sintering. Grain contact is required to check particle growth and later coalescence, and the contacts are enhanced by thermal motion, and gravity. Courtney [10] has developed a systematic analysis of contact formation process based upon Brownian motion for the system with a low volume fraction of solid. It is found that the particle growth at the early stage of liquid phase sintering is controlled by coalescence; however, after a sufficient sintering period, e.g. 10 min, a rigid microstructure is developed which inhibits the new contacts, and thus reduces the possibility of coalescence. Because the annealing times in this study are much longer, the coalescence process should not be too significant during liquid phase sintering. Moreover, Makarova *et al.* [11] found that the measured percentage of solid grain pairs decreased with prolonged sintering for the system of 90W–7Ni–3Fe. This observation is contrary to the prediction of coalescence process, in which the connectivity and contiguity of grains should be increased as coalescence progresses. In addition, a stationary size distribution is observed in this investigation for the specimens

TABLE II The α values of the chi-square statistical test for the goodness of fit between the observed and theoretical size distributions of reaction control (R) and diffusion control (D) predicted by LSW

Time (min)	Composition (wt %)									
	90W–5Ni–5Fe		92W–4Ni–4Fe		95W–2.5Ni–2.5Fe		97W–1.5Ni–1.5Fe		90W–7Ni–3Fe	
	R (%)	D (%)	R (%)	D (%)	R (%)	D (%)	R (%)	D (%)	R (%)	D (%)
10	69	3	98	0	87	0	43	0	94	0
30	21	2	–	–	82	0	48	0	–	–
60	88	1	34	0	90	0	84	0	79	0
120	31	0	–	–	75	4	8	0	19	1
300	88	0	99	0	99	0	70	0	24	0
480	2	0	32	0	2	0	86	0	85	0

annealed at 1450° C for 10 to 480 min, providing further evidence that the particle growth is dominated by the process of Ostwald ripening rather than coalescence. Therefore, the analysis of particle growth using these theories developed by LSW or Ardell for Ostwald ripening in this study, is reasonable.

The observed growth isotherms in Fig. 3 and the variation of growth rate with the volume fraction of tungsten in Fig. 4 are consistent with the theoretical predictions of the diffusion-controlled mechanism in the theories of LSW [1, 2] and Ardell [4]. However, the obtained particle size distributions agree significantly with the reaction-controlled distribution of LSW. These results can be explained by Ardell's theory, in which the effect of volume fraction of solid on coarsening kinetics has been considered. It is predicted by Ardell's analysis that the cubic rate law is still valid for the diffusion-controlled growth, even though the corresponding particle size distribution resembles that of reaction controlled distribution of LSW. The experimental results observed in this study are basically consistent with those found in W–Ni by Kang and Yoon [12].

5. Conclusions

Coarsening kinetics of tungsten particles in W–Ni–Fe alloys during liquid phase sintering has been studied. High sintered densities, > 99% theoretical density, and spherical tungsten grains uniformly distributed in the matrix phase are observed for the specimens fired at 1450° C for 10 to 480 min. The growth isotherms follow the cubic rate law and the growth rate increases with increasing the volume fraction of tungsten, which are in agreement with the diffusion-controlled growth predicted by the theories of LSW and Ardell. However, the observed particle size distributions are significantly best fitted by the reaction-controlled curve of LSW, determined by a chi-square statistical test. These observations are consistent with the prediction of diffusion-controlled growth in Ardell's theory.

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