Abnormal Growth of Faceted (WC) Grains in a (Co) Liquid Matrix

YOUNG JOON PARK, NONG MOON HWANG, and DUK YONG YOON

If the grains dispersed in a liquid matrix are spherical, their surface atomic structure is expected to be rough (diffuse), and their coarsening has been observed to be controlled by diffusion in the matrix. They do not, furthermore, undergo abnormal growth. On the other hand, in some compound material systems, the grains in liquid matrices are faceted and often show abnormal coarsening behavior. Their faceted surface planes are expected to be singular (atomically flat) and therefore grow by a defect-assisted process and two-dimensional (2-D) nucleation. Contrary to the usual coarsening theories, their growth velocity is not linearly dependent on the driving force arising from the grain size difference. If the growth of the faceted grains occurs by 2-D nucleation, the rate is expected to increase abruptly at a critical supersaturation, as has been observed in crystal growth in melts and solutions. It is proposed that this growth mechanism leads to the abnormal grain coarsening. The 2-D nucleation theory predicts that there is a threshold initial grain size for the abnormal grain growth (AGG), and the propensity for AGG will increase with the heat-treatment temperature. The AGG behavior will also vary with the defects in the grains. These predictions are qualitatively confirmed in the sintered WC-Co alloy prepared from fine (0.85-μm) and coarse (5.48-μm) WC powders and their mixtures. The observed dependence of the AGG behavior on the sintering temperature and the milling of the WC powder is also qualitatively consistent with the predicted behavior.

I. INTRODUCTION

THE shape of the grains dispersed in liquid matrices in materials prepared, for instance, by liquid-phase sintering is either nearly spherical with smoothly curved surface or faceted with flat planes. These grains coarsen during the heat treatment at temperatures above the melting point of the matrix phase. While those alloys with spherical grains undergo normal Ostwald ripening, those with faceted grains often show abnormal growth. The purpose of this work is to examine the mechanism of the abnormal growth of these faceted grains in liquid matrices, as related to the grain surface structure and the growth mechanisms which have been extensively studied for the crystal growth in melts and solutions.

In such metallic systems as W-Ni-Fe,[1,2] W-Ni,[3] Mo-Ni,[4] Co-Cu,[5] and Fe-Cu,[6] but also in some oxides such as ZnO,[7,8] MgO,[9] and Zr$_2$O$_3$,[10] and in carbides such as VC-Co[11] and Mo$_2$C-Co,[12] prepared by liquid-phase sintering, the grains in liquid matrices are nearly spherical if the liquid volume fractions are sufficiently high. The spherical grains represent the equilibrium shape, which in turn implies isotropic interfacial energy. This conclusion was confirmed by observing the spherical liquid droplets trapped in the grains.[7,13] The observed spherical shape of liquid droplets trapped in the grains implies that the spherical grains represent the equilibrium shape and that the interfacial energy is isotropic.

The isotropic surface energy in turn implies an atomi-cally rough (or diffuse as sometimes referred to) surface. Because the atom attachment or detachment at a diffuse surface is sufficiently rapid to maintain local equilibrium, the grain growth is diffusion controlled, as is indeed verified experimentally in several of these systems.[3,5,6,11,12,14–16] The spherical grain shape is therefore consistent with diffusion-controlled coarsening. As theoretically predicted,[17–23] the material systems with spherical grains were found to reach the steady state of an invariant with the normalized size distribution.[3,5,6,24] The geometrical similarity was thus maintained. In particular, no abnormal grain coarsening has been observed in these alloys.

Some crystals were also believed to grow from their melts with diffuse surface structures. The growth of tin, cyclohexanol, and succinonitrile crystals[25] was observed to occur at finite observable rates, even at very small undercoolings in the order of 10^{-3} K, and the growth rates increased linearly with the degree of undercooling.[25–28] In these cases, it was believed that there was little barrier to the atom attachment to the diffuse surface.

In some compound systems, such as WC-Co,[29–33] TaC-Co, TiC-Co, and HfC-Co[12] and Si$_3$N$_4$,[34] MgAl$_2$O$_4$,[35] and BaTiO$_3$,[36] the grains dispersed in liquid matrices are faceted with flat surface planes. Because these planes are likely to be atomically smooth, the atom attachment to them will be restricted under normal conditions. On the basis of the experimental observations,[12] it has been suggested that the grain coarsening in these systems is controlled by interface reaction. Warren and Waldron[12] observed that the grains in VC-Co and Mo$_2$C-Co were nearly spherical, and their coarsening behavior agreed with that predicted for the diffusion-controlled mechanism. They observed, on the other hand, that the grains in TaC-Co, TiC-Co, and HfC-Co were faceted with {100} surfaces, and their coarsening rates were much lower and the activation energies higher than those measured in VC-Co and Mo$_2$C-Co. It was observed, fur-

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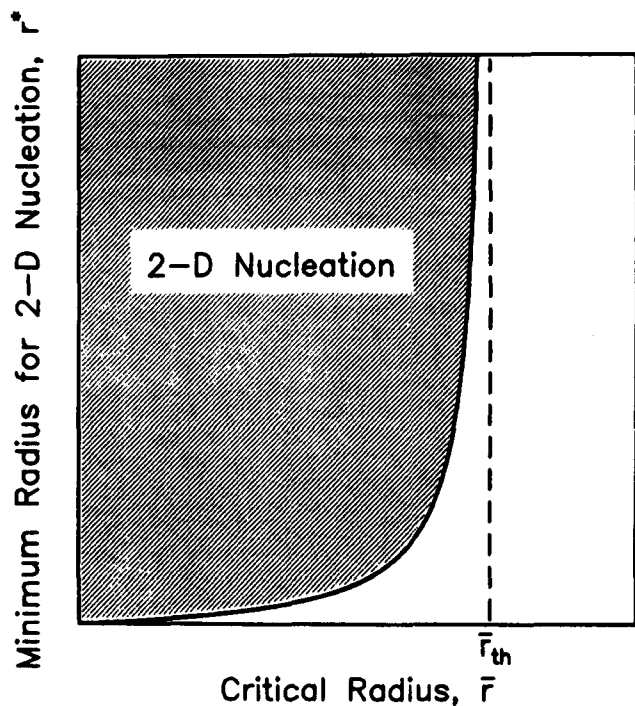
Fig. 1—Schematic dependence of the minimum grain radius required for 2-D nucleation on the critical grain radius.

thermore, that the coarsening rates of the faceted grains were nearly independent of the matrix volume fraction. As suggested by Warren and Waldron, these results indicate that the coarsening of the faceted grains in TaC-Co, TiC-Co, and HfC-Co is controlled by interface reaction. (The results for NbC-Co[37,38] were somewhat inconclusive.) Similar evidence for the interface-controlled coarsening was found for WC-Co. The coarsening rate (except for those grains growing abnormally) is relatively low with high values for the activation energy[31,39,40] and does not decrease with increasing Co content.[39,41-43] An additional characteristic behavior of many of the material systems (including WC-Co) with faceted grains is that they show abnormal grain growth (AGG)[29-33,36,44-50] while those with spherical grains do not, as noted earlier.

In the theoretical treatments of the interface-controlled Ostwald ripening,[18] the growth velocity is usually assumed to depend linearly on the driving force, which is determined by the grain size difference. It is predicted, as in the diffusion-controlled coarsening, that the system will reach a steady state where the normalized grain size distribution remains invariant. This grain size distribution is predicted to be relatively narrow with the largest grain about 2.25 times larger than the average size. No abnormal coarsening is predicted even when the initial grain size distribution is bimodal.[51]

A clue to understanding the abnormal growth of the faceted grains may be found in the mechanisms for the growth of the crystals with faceted surface planes from a melt or a solution. It was proposed[52-57] and demonstrated experimentally[25,26,58-61] that the melt and the solution growth of the crystals with singular planes occurred by defect-promoted mechanisms and two-dimensional (2-D) surface nucleation. The same mechanisms may be operating in the coarsening of the faceted grains in a liquid matrix and may

cause these grains to grow abnormally. Such a possibility is explored in this work.

The abnormal growth of grains dispersed in a matrix may be defined as the case where the grain size distribution becomes wider than those predicted by the usual Ostwald ripening theories. The geometrical self-similarity may also be violated. Although the real size distribution of the grains with complex shapes is difficult to determine, a small fraction of the grains is sometimes observed to be so much larger than the rest that the abnormal growth can be unambiguously identified. The AGG in sintered WC-Co is such a case.[29-33] In this work, initial powder size, heat-treatment temperature, and initial ball-milling are identified in the defect and 2-D nucleation theory as the key process variables for the AGG and their effects are experimentally determined in WC-Co for comparison with the theoretical predictions.

II. ABNORMAL COARSENING BY 2-D NUCLEATION

For a system of grains dispersed in a liquid matrix, the driving force Δg_r for the growth of a grain with an effective radius r and average surface energy σ is

$$\Delta g_r = 2\sigma V_m \left(\frac{1}{\bar{r}} - \frac{1}{r} \right) \qquad [1]$$

where V_m is the molar volume of the solid phase and $\bar{r}$ is the critical radius of the grain which does not grow or shrink. If the grains are faceted and therefore their growth is limited by 2-D nucleation, the growth rate of a grain with a radius r will be[52,53,57]

$$\frac{dr}{dt} = A \exp \left\{ \frac{-\pi h \sigma}{2\left(\frac{1}{\bar{r}} - \frac{1}{r}\right)kT} \right\} \qquad [2]$$

In this equation, A is a product of material constant and $\exp(-\Delta G_m/kT)$, where ΔG_m is the activation energy for jumping across the interface. For those grains with sizes larger than a minimum value r^*, the driving force will exceed the minimum value Δg_r^* required for rapid growth by 2-D nucleation. Thus . . .

$$\Delta g_r^* = 2\sigma V_m \left(\frac{1}{\bar{r}} - \frac{1}{r^*} \right) \qquad [3]$$

This relationship between $\bar{r}$ and r^* for a certain value of Δg_r^* is schematically shown in Figure 1. The growth by 2-D nucleation will occur in the 2-D nucleation region above the curve in Figure 1. For a given $\bar{r}$, those grains larger than r^* will grow by 2-D nucleation, and conversely, for a grain of size r^* to grow by 2-D nucleation, there is a maximum value of $\bar{r}$. Because an abnormally large grain will have a size much larger than $\bar{r}$, Δg_r^* can be approximated by

$$\Delta g_r^* \approx \frac{2\sigma V_m}{\bar{r}_{th}} \qquad [4]$$

This threshold critical size $\bar{r}_{th}$ is obtained for $r^* = \infty$, as shown in Figure 1, and represents the effective $\bar{r}$ required for 2-D nucleation in the grains much larger than $\bar{r}$. For an

abnormally large grain of finite size, the value of $\bar{r}$ required for 2-D nucleation will be slightly smaller than $\bar{r}_{th}$. If $\bar{r} > \bar{r}_{th}$, the growth by 2-D nucleation is impossible for any grain.

It is now necessary to re-examine the term $\bar{r}$ when the growth occurs by 2-D nucleation. In the usual theories of interface-controlled Ostwald ripening,[18,20] the growth rate dr/dt of a grain is assumed to be linear in Δg_r. From the condition that the total amount of the solid phase remains constant and hence the total flux to the grains is 0, $\bar{r}$ is predicted to be equal to 9/8 of the average size for the invariant normalized size distribution.[18]

When the equilibrium shape of grains is faceted, the mechanism for the growth may be different from that for the dissolution. Therefore, the functional dependence of dr/dt on $(1/\bar{r} - 1/r)$ may be different for the growing and shrinking grains. Nevertheless, because the total solid content is assumed to remain constant, the total atom flux to the growing grains will be always equal to that from the shrinking ones, and therefore, there will always be a grain of $\bar{r}$, which neither grows nor shrinks. Because the dependence of dr/dt on $(1/\bar{r} - 1/r)$ is not exactly known for the shrinking and growing grains, the value of $\bar{r}$ can be assessed only qualitatively. It has been proposed that the dissolution at the singular surface occurs by detachment of atoms at the edges to produce surface steps and kinks, which move across the surface to remove the atom layer.[57] The kinetics of such a process is expected to be much faster than the growth by 2-D nucleation. If the dissolution kinetics is much faster than the growth kinetics, $\bar{r}$ is expected to be smaller than that predicted in the usual Ostwald ripening theory. But the growth kinetics of those grains larger than r^* also will be fast. The presence of these rapidly growing large grains will tend to shift $\bar{r}$ to a large size. Thus, the value of $\bar{r}$ is difficult to estimate, but in the initial stage where the grains largely retain the size of the particles in the powder without any significant growth, $\bar{r}$ is expected to be close to the average size. Equation [4] can then be interpreted to indicate that there is a threshold average size of the initial particles for AGG growth by 2-D nucleation. If the initial size distribution is bimodal, $\bar{r}$ may be determined largely by the fine grains, because they are more numerous and rapidly dissolving.

The critical driving force Δg^* required for crystal growth from a melt is

$$\Delta g^* = \frac{\Delta H \Delta T}{T_m} \qquad [5]$$

where ΔH is the latent heat of fusion per mole, ΔT the supercooling, and T_m the melting temperature. The values of Δg^* for the melt growth of crystals with singular surfaces have been experimentally determined for several material systems.[25,26,59,60] The measurement of Peteves and Abbascian[60] shows that ΔT required for the growth of a Ga crystal by 2-D nucleation is 1.5 K, which gives $\Delta g^* = 30$ J/mol. Assuming that same critical driving force is required for 2-D nucleation in coarsening, Eq. [4] gives $\bar{r}_{th} = 0.67$ μm, using a typical value of 1 J/m^2 for σ and 10^{-5} m^3 for V_m. Because Δg^* varies with the material system and the temperature, such an estimation of $\bar{r}_{th}$ from the solidification data of Ga will be significant only in the order of magnitude when applied to grain coarsening.

The coarsening grains or a growing crystal may contain such defects as screw dislocations, edge dislocations, and twin boundaries which promote the growth, even at low supersaturations by forming surface ledges.[55,56,62-65] Screw dislocations will cause the well-known spiral growth, with its rate initially varying parabolically as the supersaturation increases.[56,60,66] The rate of the defect-promoted growth will increase with the defect concentration. At a high dislocation density, the growth rate will increase to the growth rate of a diffuse surface even before the supersaturation increases to Δg^*. If the dislocation density is low, the growth rate will increase at first slowly with the supersaturation and then sharply to the growth rate of a diffuse surface near Δg^*. For a defect-free grain, the growth rate will be almost 0 at low driving forces and abruptly increase near Δg^*.

III. EXPERIMENTAL

The prediction on the basis of $\bar{r}_{th}$ that the occurrence of AGG critically depends on the initial grain size was tested on liquid-phase sintered WC-Co using WC powders of 0.85 and 5.48 μm in average size, as measured by a Fisher subsieve sizer. The WC powder was mixed with 15 wt pct of Co powder in ethyl alcohol without milling. After evaporating the alcohol at 80 °C, the powder mixture was pressed under 50 MPa into cylindrical compacts of 10 mm in diameter and about 6 mm in height. The compacts were presintered at 900 °C for 1 hour and sintered at either 1500 °C or 1600 °C in a carbon crucible filled with carbon powder under flowing hydrogen. The polished specimens were etched in Murakami solution.[67] The grain size distributions were determined on optical and scanning electron micrographs by measuring the grain areas and, thereby, the equivalent spherical diameters using a digitizer connected to a personal computer. These measurements were made on about 400 grains randomly selected for each specimen.

IV. RESULTS AND DISCUSSION

A. Fine WC Powder

As shown in Figure 2, the particles in the WC powder of 0.85 μm in average size were mostly smaller than 1 μm, but appeared to have formed agglomerates, and a small fraction of the particles appeared to be larger than 1 μm. The evolution of the grain structure during sintering of the compacts prepared from this 0.85-μm WC powder at 1500 °C is shown in Figure 3. After sintering for 5 minutes, some abnormally large grains with apparent lengths exceeding 10 μm were observed, as shown in Figure 3(a). Their number density varied from one region of the specimen surface to another, and there were on the average about four of such large grains per 1 mm^2 area. During sintering for 30 minutes, the size of the large abnormal grains increased. Upon further sintering, the abnormal grains grew further, as shown in Figures 3(c) through (e). After sintering for 5 minutes and 5 hours, the largest grains had average lengths of about 15 and 130 μm, respectively. The apparent number density of these large grains steadily increased during sintering to about 10 per mm^2 after 5 hours. It is possible that the actual number of large grains did not increase during
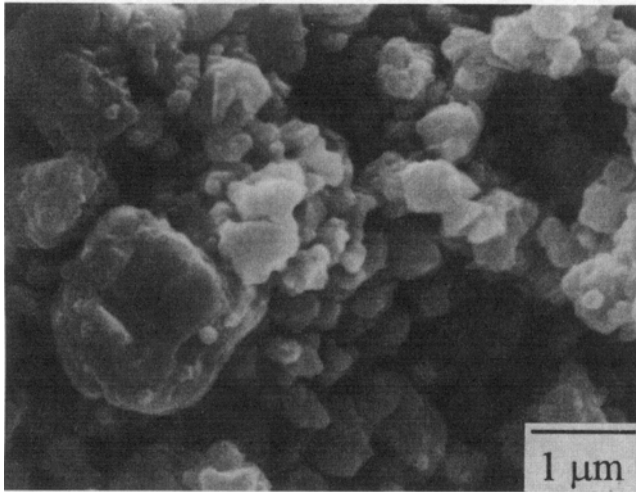
Fig. 2—The scanning electron microstructure of the WC powder of 0.85-μm average size.

sintering past the initial 5 minutes, because the apparent increase of the number density can be attributed to the increasing probability of intersecting them at cross sections as they grew in size.

During the sintering treatment, the fine grains also coarsened, as shown in Figures 3(a) through (e). After sintering for 30 minutes, grains slightly larger than the initial powder size with distinctively faceted shapes appeared, as shown in Figure 3(b). These grains had mostly elongated shapes with the long faces parallel to each other, and their size increased steadily as verified by the measured grain size distributions. Figure 4 shows the histogram of the grain size distribution for the specimen of Figure 3(e). The abnormally large grains had an average diameter of about 35 μm, and these had grown from grains about 25 μm in diameter after sintering for 1 hour, as shown in Figure 3(c).

The observed elongated shapes of the large and intermediate size grains appear to represent the cross sections of the truncated flat triangular prisms which have been observed for the extracted grains in this alloy.[32,39,68,69] Because such shapes are observed under various sintering conditions, they may resemble an equilibrium shape, but if their growth is controlled by interface reaction, the growth rate is expected to also be anisotropic and may hence influence the shape. If the growth occurs by 2-D nucleation, the rate anisotropy is difficult to predict, because the orientation dependence of the step energy is difficult to take into account. The observed grain shapes might still be close to that of the equilibrium, because the material transfer from one surface to another of the same grain may slowly occur by a defect-assisted process under relatively low driving forces. The fine grains might be more equiaxial, either because they are closer to the equilibrium due to their size or because they are dissolving.

The observed AGG in this powder compact of 0.85-μm powder size is consistent with the prediction that AGG will occur if the average grain radius is smaller than the threshold value $\bar{r}_{th}$, which was estimated to be 0.67 μm, or 1.34 μm for the diameter. A quantitative comparison between the observed and predicted threshold values is not, however, very significant, because the actual powder size and its distribution cannot be adequately represented by the average size, and the theoretical estimate is not expected to be very accurate, as discussed earlier. The overall coarsening behavior, including the appearance of the intermediate size grains, appears to be qualitatively consistent with the process promoted by defects and 2-D nucleation. For the coarsening behavior, the supersaturation for each grain of radius r is defined as $\Delta g_r = 2\sigma V_m (1/\bar{r} - 1/r)$. In the initial stage of sintering, those grains with radii exceeding the minimum radius r^*, which is estimated to be about 1.17 μm from Eq. [3] for $\Delta g_r^* = 30$ J/mol and $\bar{r} = 0.425$ μm, would have grown by 2-D nucleation to abnormally large sizes. As they began to grow, the driving force for their further growth would have also increased, resulting in accelerated growth. The grains are also likely to contain defects such as dislocations and twin boundaries. It is then possible that the larger grains in the powder, which were smaller than r^*, might have initially grown by the defect-assisted process and then by 2-D nucleation after exceeding r^*. If the defect density varied from one grain to another, those grains with higher defect density would have been more prone to undergo such a rapid growth. Thus, a few large grains, possibly with high defect density, could have undergone accelerated growth to become the abnormally large grains.

Those grains only slightly larger than the average size or with relatively low defect density might have grown more slowly to become the intermediate size grains. The fine grains also grew, although much more slowly than the larger ones, and their growth would also have been assisted by the defects. The growth of the fine grains would have caused a steady decrease of the driving force for growth of the large grains, and at some stage, which might be after sintering for 2 hours (Figure 3(d)), the average grain size probably became larger than the threshold value $\bar{r}_{th}$, which was estimated to be 0.67 μm. Then, even the abnormally large grains could no longer grow by 2-D nucleation and might have grown more slowly again by the defect-assisted process. The observed overall coarsening behavior thus appears to agree qualitatively with that expected of grains of varying size and defect density.

Previous observations also show that AGG occurs when fine WC powders are used.[30,32,33] Schreiner et al.[29] observed that when 1-μm WC powder was used after milling, there was a slight tendency for AGG after sintering at 1430 °C (the sintering duration was not specified) and pronounced AGG after sintering at 1500 °C. Similarly, Eun[32] observed pronounced AGG in the specimens prepared from a 0.9-μm WC powder which was wet ball-milled after mixing with Co powder and sintered at 1500 °C for 3 minutes and 50 hours. In another experimental series, Eun observed that specimens prepared from a WC powder of 3-μm average size, but containing agglomerates of submicron size grains, showed AGG after sintering at 1500 °C. All previous observations, as well as the present one, thus show that AGG occurs in WC-Co if the WC powder contains a substantial amount of submicron size grains, as predicted by the 2-D nucleation theory.

The condition for the growth by 2-D nucleation will vary with the material properties. In particular, the threshold average grain size $\bar{r}_{th}$ for AGG is predicted to vary inversely with σ. Therefore, the additives may alter the AGG behavior through their effect on σ, as observed in WC-Co.[31,70] The dependence of the AGG behavior on the powder size
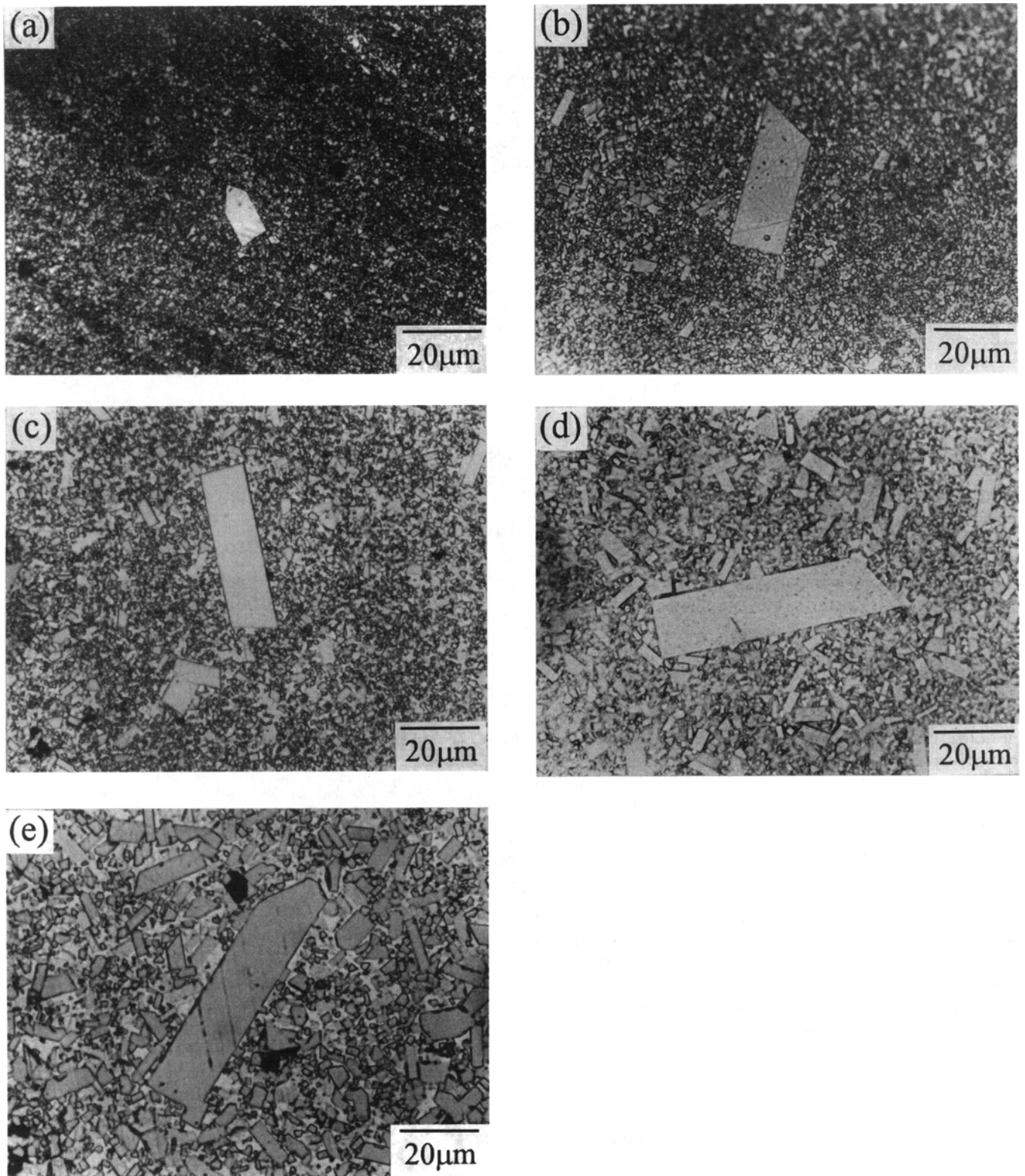
Fig. 3—The microstructures of the WC-15 wt pct Co specimens prepared from a 0.85-μm WC powder sintered at 1500 °C for (a) 5 min, (b) 30 min, (c) 1 h, (d) 2 h, and (e) 5 h.

can, however, be quite complex. If the powder size exceeds $\bar{r}_{th}$, no AGG will occur, as discussed earlier. If the powder size is smaller than $\bar{r}_{th}$ and there are only a few large grains, they can grow abnormally to very large sizes. If the powder is even finer, or the large grains are numerous, there will be many abnormally growing grains, but their size will be limited because of the reduced solute flux per abnormally growing grain.
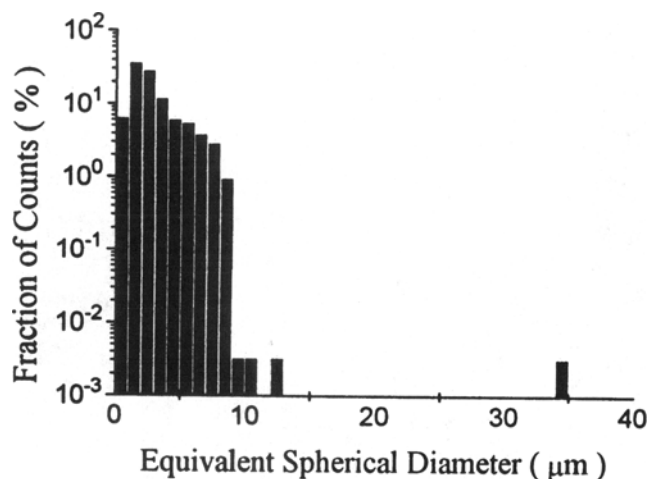
Fig. 4—The grain size distribution in the specimen prepared from 0.85-μm WC powder sintered at 1500 °C for 5 h shown in Fig. 3(e).

B. *Coarse WC Powder*

In order to test the prediction that the growth by 2-D nucleation will not occur if the average grain size is larger than the threshold radius $\bar{r}_{th}$, which was estimated to be 0.67 μm, the next series of specimens was prepared from a coarse WC powder of 5.48-μm average size. No AGG was observed after sintering for 10 minutes at 1500 °C, as shown in Figure 5(a). After sintering for 1/2, 1, and 20 hours, there was almost no change of the grain structure and possibly a slight coarsening, as shown in Figure 5(b). The grain size distribution for the specimen sintered for 1/2 hour is shown in Figure 7(b) and its microstructure in Figure 6(d). Figure 7(b) shows a typical normal size distribution. The predicted absence of AGG in these specimens was thus confirmed. Although some of the grains appeared to be as large as about 10 μm, as shown in Figure 5(a), the driving force for their coarsening would have been very small because of the large average grain size. Therefore, although these grains might have also contained some defects, their growth would have been extremely slow, as confirmed by the observations. Previous observations also showed that no AGG occurred if a coarse WC powder was used.[30,32] Eun,[32] for example, observed that the specimens prepared from a WC powder of 10.4-μm size did not show any AGG after sintering at 1450 °C for 1 hour.

In the next experimental series, fine (0.85-μm) WC powder was mixed with coarse (5.48-μm) WC powder at the ratios of 9/1, 7/3, 3/7, and 0/10 by weight to test the possibility that the coarse grains grow abnormally if surrounded by fine ones. For the average size of 0.85 μm, the minimum radius r^* for 2-D nucleation was estimated to be about 1.17 μm from Eq. [3], as described earlier. Because most of the grains in the 5.48-μm powder were larger than this size, they were expected to grow abnormally by 2-D nucleation. After sintering for 30 minutes at 1500 °C, the specimen of 90 pct 0.85-μm and 10 pct 5.48-μm WC powders (Figure 6(a)) showed a typical AGG structure, with some grains clearly larger and more elongated than those in the specimens prepared from only 5.48-μm WC powder shown in Figures 5(a), 5(b), and 6(d), as confirmed by comparing the histograms shown in Figures 4 and 7(a). The number density of the abnormally large grains in this spec-
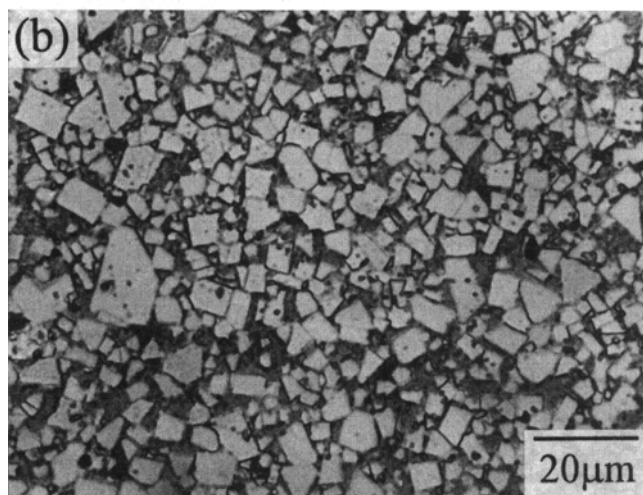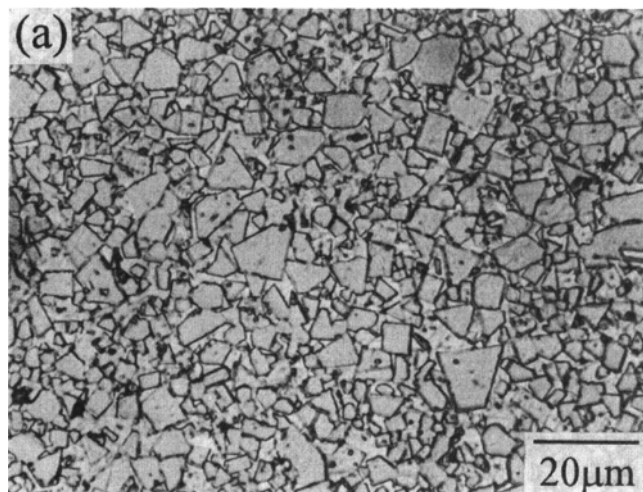

Fig. 5—The microstructures of the specimens prepared from a 5.48-μm WC powder sintered at 1500 °C for (a) 10 min and (b) 20 h.

imen was much larger than that in the specimen prepared from only 0.85-μm powder (Figure 3(b)) and appeared to be approximately equal to the number density of the 5.48-μm grains. At the stage of sintering shown in Figure 6(a), the fine grains still remained to cause the rapid growth of the large grains by 2-D nucleation, as shown in Figure 8, after sintering further for 2 hours. As shown in Figure 3(d), the specimen prepared from only 0.85-μm powder showed much lower number density of the abnormally large grains also at this stage of sintering.

The number density of the abnormal grains in the specimen prepared from a mixture of 70 pct 0.85-μm powder and 30 pct 5.48-μm WC powder was larger than that in the specimen with 10 pct 5.48-μm WC powder, as shown in Figure 6(b). After sintering for 30 minutes, the volume fraction of the very fine grains appeared to have decreased from the initial value of 70 pct as they dissolved and reprecipitated on the large grains. The specimen prepared from a mixture of 30 pct 0.85-μm powder and 70 pct 5.48-μm powder sintered for 30 minutes showed more abundant large grains, as shown in Figure 6(c), but their size was smaller than those in the specimens containing 10 and 30 pct 5.48-μm powder (Figures 6(a) and (b) respectively). It also appeared that most of the very fine grains were dis-
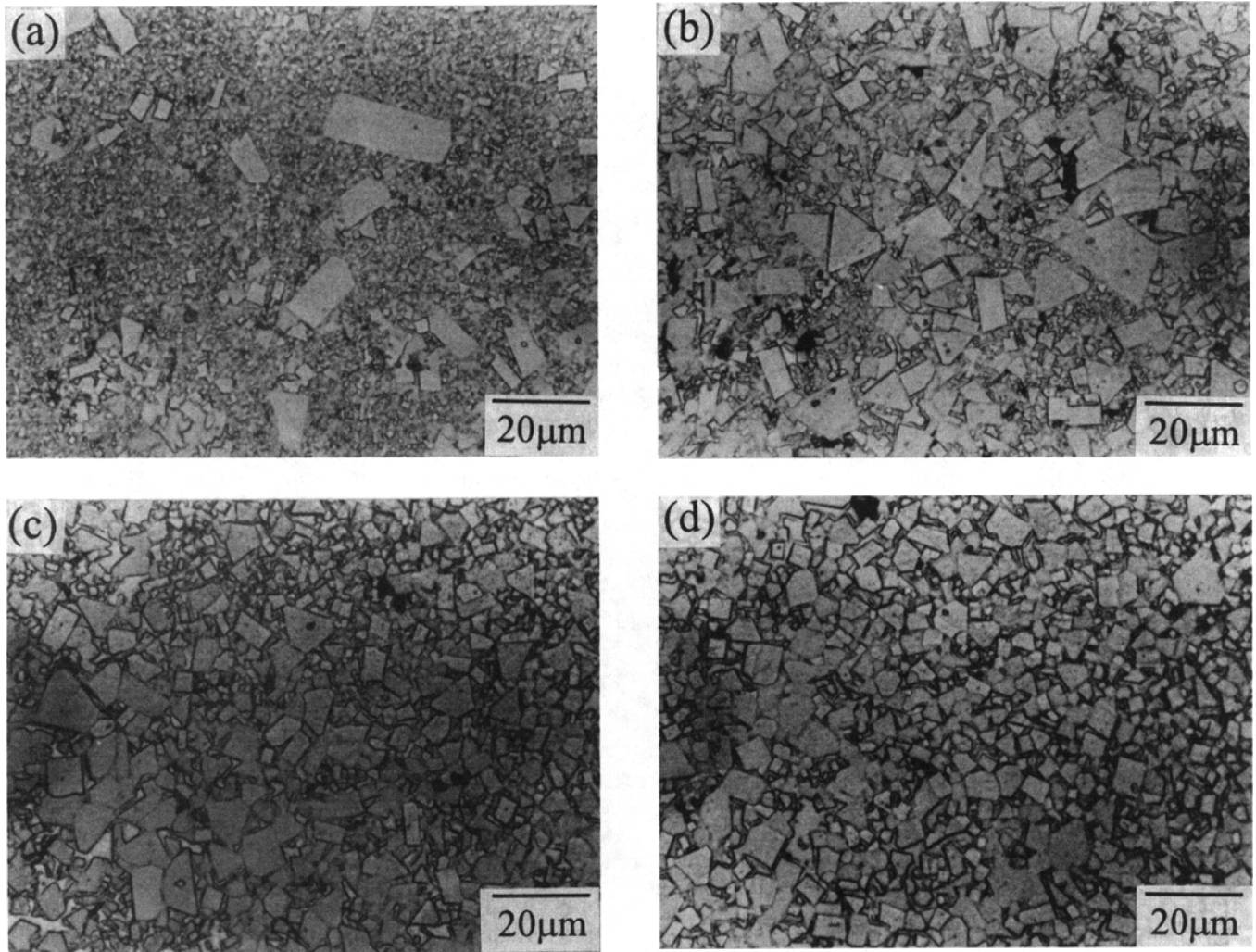
Fig. 6—The microstructures of the specimens prepared from mixtures of fine (0.85-μm) and coarse (5.48-μm) WC powders at respective weight percents of (a) 90:10, (b) 70:30, (c) 30:70, and (d) 0:100 and sintered at 1500 °C for 30 min.

solved in this specimen. In this specimen, it is possible that in the initial stage with still abundant fine grains, the driving force for coarsening was large enough to induce the growth by 2-D nucleation of the numerous large grains, but when the fine grains were consumed, the driving force might have been reduced again below the critical value for 2-D nucleation at the sintering stage shown in Figure 6(c). Then, even the large grains may grow slowly by a defect-assisted process upon further sintering. The specimen prepared from only 5.48-μm powder had a grain structure (Figure 6(d)) which did not change noticeably during sintering, as described earlier with Figures 5(a) and (b). The histogram shown in Figure 7(b) exhibited a typical normal grain size distribution.

The variation of the AGG behavior with the volume fraction of the coarse grains shown in Figures 6(a) through (d) is essentially identical to the earlier observations of Eun[32] and Schreiner et al.[29] These results show that the coarse grains become the seeds for AGG, as predicted by the 2-D nucleation model. It appears that the abnormally grown grains are larger in the specimens with less coarse powder as shown in this series, because the solute flux for the abnormal growth has to come from the fine grains. These observations with initially bimodal grain distributions thus

indicate that AGG occurs by the rapid growth of large grains and dissolution of the fine ones, until the fraction of the fine ones becomes too small to induce the growth by 2-D nucleation.

In contrast to this AGG behavior during the sintering of WC-Co, when fine (10 μm) W powder mixed with spherical large W particles of about 200-μm diameter was liquid-phase sintered at 1670 °C after adding 4 wt pct of Ni, the fine grains grew more rapidly than the large ones until the overall size distribution approached that of steady-state Ostwald ripening.[71] As discussed in Section I, the grains in this W-Ni alloy with a nearly spherical shape and an atomically diffuse surface structure coarsen by a diffusion-controlled process. These contrasting behaviors of the large grains embedded in fine grains of the W-Ni and WC-Co systems provide additional evidence for the proposal that the occurrence of AGG depends on the growth mechanism.

The AGG in a polycrystalline single-phase system has been theoretically analyzed and simulated by Hillert[72] and others.[72-78] Although in this case the material transfer occurs only between the neighboring grains, the growth of a grain may be assumed to be influenced by the others located far away through the interaction with the neighboring ones. It may then be assumed, as did Hillert, that each grain
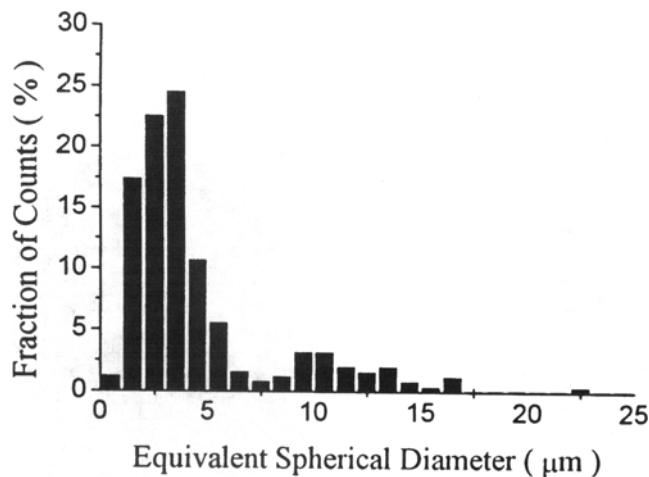
(a)
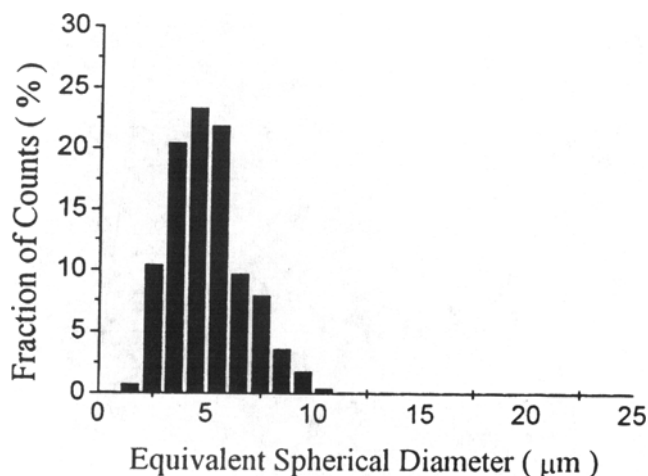
(b)

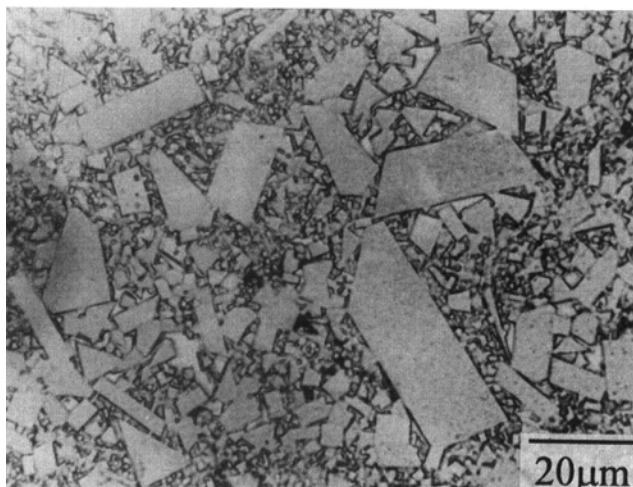Fig. 7—The grain size distribution of the specimens shown in (a) Fig. 6(a) and (b) Fig. 6(d).

Fig. 8—The microstructure of the specimen prepared from a mixture of fine (0.85-μm) and coarse (5.48-μm) WC powders at weight percents of 90:10 and sintered at 1500 °C for 2 h.

is surrounded by its neighbors whose average size is equal to the average of all grains. The theoretical treatment in this mean field formalism then becomes identical to that for the

interface-controlled growth of the grains dispersed in a matrix. Initially, Hillert misinterpreted the results of his analysis to predict that if there are grains which are larger than twice the average radius, they will grow abnormally. But Thompson et al.[51] subsequently showed that such large grains grow more slowly than those of the average size. Therefore, a system with initially a bimodal size distribution will attain a normal distribution without undergoing an abnormal growth. This conclusion was confirmed by the Monte Carlo simulation of Srolovitz et al.[76] These analyses thus show that no AGG is expected if the growth velocity is assumed to be linear to the driving force arising from the size difference.

Various models have been used for the simulation of AGG in polycrystalline systems.[51,72–78] The computer simulation and the analytical solutions of Rollet et al.[73] show, as would be expected, that if the abnormal grains have a higher mobility than the normal grains, AGG will occur. Although such a model may apply to the randomly oriented abnormal grains embedded in highly textured normal grains, it cannot be valid for the WC-Co alloy where the grains are randomly oriented and the material transfer occurs among many grains through the liquid matrix. The model itself, however, has some similarity to the defect-assisted and 2-D nucleation growth theories, where the large grains may be viewed as having, in effect, high mobilities.

V. TEMPERATURE DEPENDENCE

The growth rate of a singular interface assisted by 2-D nucleation or defects will increase with temperature because of the increasing atom transfer rate to the surface steps and over the nucleation energy barrier. Because Δg^* will decrease with increasing temperature, for the same $\bar{r}$, r^* will decrease in accordance with Eq. [3], and $\bar{r}_{th}$ will increase in accordance with Eq. [4] as the temperature increases. This means that there will be more grains which can grow by 2-D nucleation at higher temperatures. It is still possible, as discussed earlier, that the abnormally growing grains are selected on the basis of their defect density as well as their size. Then as the grains undergo the defect-assisted growth, more of them will attain the critical size for 2-D nucleation at higher temperatures.

This prediction was qualitatively confirmed in the specimens prepared from 0.85-μm WC powder and sintered at a higher temperature of 1600 °C. As shown in Figure 9(a), the specimen sintered at 1600 °C for 5 minutes had a significantly higher number density of the abnormally large grains than those sintered at 1500 °C for 5 or 30 minutes (Figure 3(a) or (b)). The fine grains also appeared to have grown faster at 1600 °C. The increasing tendency for AGG at higher temperatures in this alloy is well known,[29,33] as observed, for instance, by Schreiner et al.[29]

A specimen prepared from the 5.48-μm powder was also sintered at 1600 °C for 30 minutes. As shown in Figure 9(b), its grain structure appeared to be identical to that sintered at 1500 °C for 10 minutes (Figure 5(a)) and again confirmed the predicted absence of AGG with such a large average grain size. The observed dependence of the AGG behavior on temperature thus appeared to be consistent with the defect- and 2-D nucleation-assisted growth.
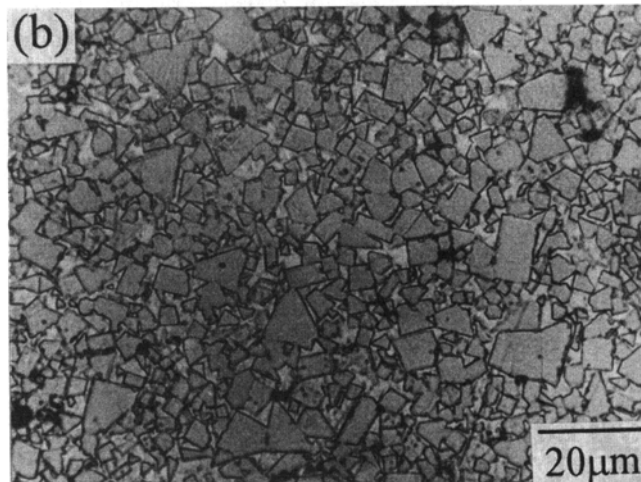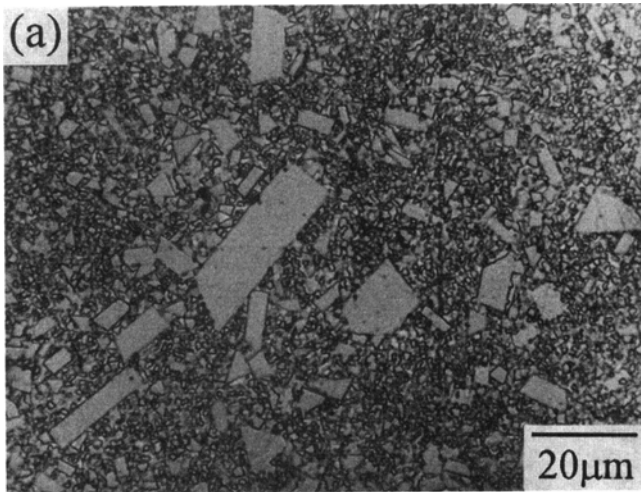
Fig. 9—The microstructures of the specimens (a) prepared from a 0.85-µm WC powder and sintered at 1600 °C for 5 min and (b) prepared from a 5.48-µm WC powder and sintered at 1600 °C for 30 min.

Fig. 10—The microstructures of the specimens prepared from a milled WC powder and sintered at 1600 °C for (a) 10 min and (b) 1 h.

VI. EFFECT OF MILLING

The 0.85-µm WC powder used in the experiments described hitherto was not milled, but the usual industrial practice of milling the WC powder may also influence the AGG behavior. In order to check this possibility, a WC powder of 3.4-µm size was ball-milled for 72 hours until its average size was reduced to 0.8 to 0.9 µm. After sintering at 1600 °C for 10 minutes, a specimen prepared from this milled WC powder had a higher number density of the large grains, as shown in Figure 10(a), than the specimen prepared from the unmilled 0.85-µm powder and sintered at 1600 °C for 5 minutes (Figure 9(a)). The large grains in Figure 10(a) and even in Figure 10(b) for the specimen sintered for 1 hour were smaller than the large grains of a limited number in Figure 9(a). The fine grains in Figure 10(a) appeared to be, on the other hand, larger than those in Figure 9(a). The specimen prepared from the milled powder had, therefore, a narrower overall grain size distribution than the specimen prepared from the unmilled fine powder.

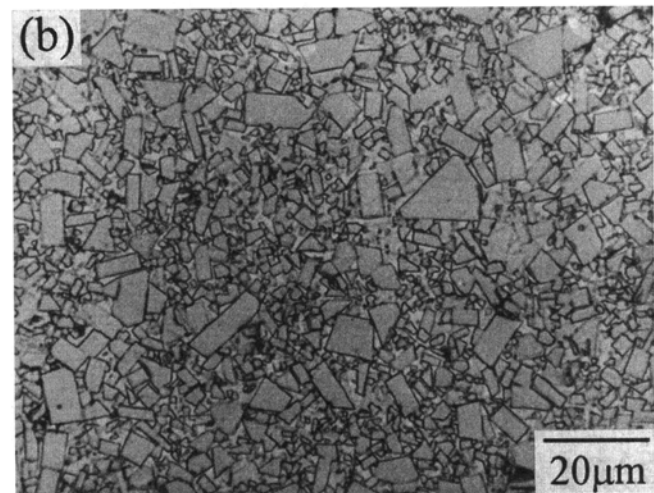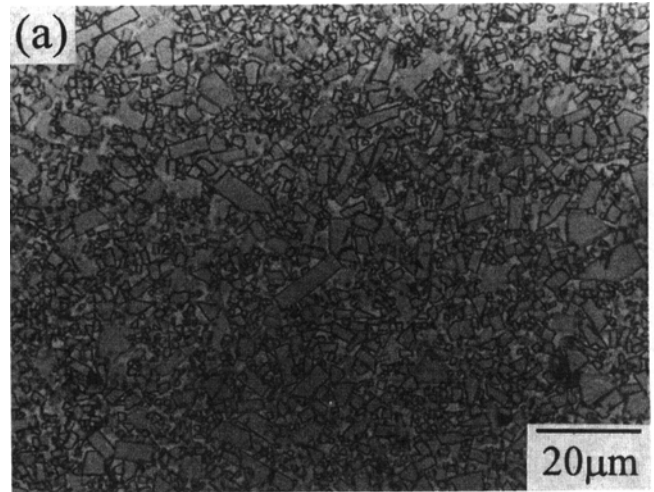The contrasting coarsening behaviors of the milled and unmilled powder may arise from the difference in the particle size distribution in the powders. Although their average sizes, as measured by a Fisher subsieve sizer, are nearly equal, a scanning electron microscopy observation indicated that the milled powder contained more coarse particles than the unmilled powder. Therefore, there may be more grains in the specimen prepared from the milled powder, which can grow abnormally because of their size advantage. When there are many growing rapidly, the material flux to each will be limited, thereby restricting their final size at each sintering stage. The observed milling effect is also consistent with the possibility that surface defects were produced in the WC powder during milling. If the defect densities in the grains are uniformly high, many grains can grow rapidly by the defect-assisted process and probably in the later stage by 2-D nucleation. The rapid coarsening of the fine grains assisted by the defects will also reduce the driving force for the growth of the large ones, again restricting their final size. The small amount of the fine WC grains in the powder may also have restricted the growth of the abnormally large grains.

In the next experimental series, the milled powder was mixed with the unmilled 0.85-µm powder at an 8/2 ratio. After sintering for 5 and 30 minutes at 1500 °C, the specimens prepared from this mixed powder had more numerous abnormally large grains, as shown in Figures 11(a) and
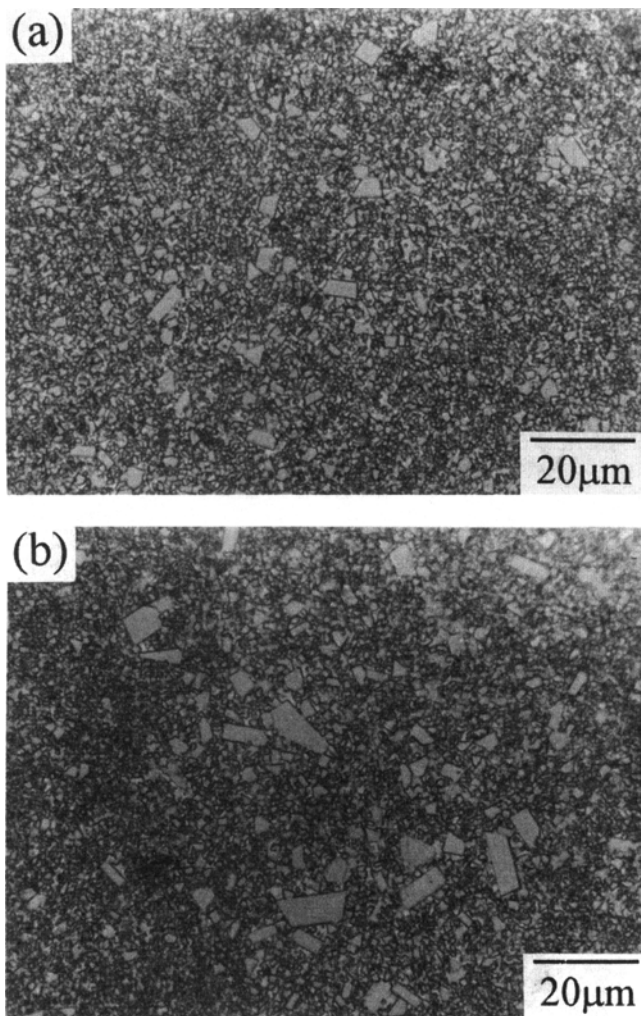
Fig. 11—The microstructures of the specimens prepared from a mixture of 80 pct unmilled 0.85-μm WC powder and 20 pct milled WC powder and sintered at 1500 °C for (a) 5 min and (b) 30 min.

2-D nucleation. Under such a condition, the abnormal growth can occur because the growth rate of a grain will vary more sharply with the driving force than the linear variation, which is assumed for the normal coarsening controlled by surface reaction. Thus, the abnormal growth of the faceted grains is entirely consistent with the present understanding of the thermodynamics and growth kinetics of the solid-liquid interface.

If the growth occurs only by 2-D nucleation, the large grains will grow rapidly to produce a bimodal overall size distribution. In the more likely case of grains with defects, the large grains and particularly those with high defect density may rapidly grow to attain the critical size for 2-D nucleation. When the number of the fine grains becomes small after rapid abnormal growth, the grains are likely to undergo defect-assisted growth again, and the overall normalized size distribution may again become narrow. The defect-assisted coarsening will depend critically on the defect type and concentration and its variation among the grains. Presently, it is unclear whether AGG can occur by defect-assisted growth without any 2-D nucleation, or if AGG will always require the 2-D nucleation. The 2-D nucleation model predicts that the propensity for AGG will increase with decreasing interfacial energy σ.

The fine initial powder size required for the abnormal growth and the seeding effect of the added large particles and milled powder appear to be strong experimental evidence for the defect and 2-D nucleation theories. The observed temperature dependence is also consistent. Until more quantitative analyses and observations are made, the logical sequence of faceted grains implying singular surface, which in turn implies defect- and 2-D nucleation-assisted growth, appears to be the most secure basis for believing in the validity of this theory.

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(b), than those prepared from only the unmilled powder (Figures 3(a) and (b)). Again, it appears that some grains in the milled powder grew abnormally because of either their size advantage or defects, and the spreading of the flux to these numerous large grains restricted their average size at each sintering stage. If some grains in the milled powder grew abnormally because of their size advantage, the observations shown in Figures 11(a) and (b) are essentially the same as those shown in Figure 6 for the mixtures containing the WC powder of 5.48-μm size. The possible effect of defects produced by milling might be verified by preannealing the WC powder or the compact before the sintering treatment.

VII. CONCLUSIONS

The fact that spherical grains in liquid matrices undergo normal diffusion-controlled coarsening, while the faceted grains undergo abnormal growth, shows that the conditions for normal and abnormal growth depend on the grain surface structure. If the grain surfaces are singular, the grains are faceted and can grow only when assisted by defects or

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